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THE USE OF SODIUM HYDROXIDE SLUGS TO

IMPROVE THE WATER FLOOD RECOVERY

OF VISCOUS CRUDE OILS

by

C HARVEY D. GARDINER

### A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

IN

PETROLEUM ENGINEERING

DEPARTMENT OF MINERAL ENGINEERING

EDMONTON, ALBERTA
Spring, 1977

# THE UNIVERSITY OF ALBERTA FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "The USE OF SODIUM HYDROXIDE SLUGS TO IMPROVE THE WATER FLOOD RECOVERY OF VISCOUS CRUDE OILS", submitted by Harvey D. Gardiner, in partial fulfilment of the requirements for the degree of Master of Science in Petroleum Engineering.



#### ABSTRACT

An experimental study was conducted to investigate the effects on water flood recovery caused by adding sodium hydroxide to a portion of the injected fluids. The investigation was conducted using actual reservoir fluids from the Lloydminster area in an unconsolidated porous medium.

Measurement of the sand and fluid properties indicated that sodium hydroxide caused a reduction of the oil-water interfacial tension and a shift in the system wettability from oil wet to neutral or water wet.

The addition of sodium hydroxide in concentrations greater than 0.1 percent by weight to all of the injected fluid (brine) resulted in recoveries of approximately 45 percent of the initial oil-in-place at a water-oil ratio of 10. Flooding with pure water resulted in recoveries of approximately 22.5 percent.

Results of the displacement tests using various size slugs of 0.1 percent sodium hydroxide indicated that slugs of approximately 0.4 pore volumes were required to obtain recoveries equivalent to adding sodium hydroxide to all of the injected fluid.

Monitoring of the pH of the effluent from the sand packs indicated that the sodium hydroxide slugs



were diluted by fingering of the untreated brine at the trailing edge. Higher concentrations of sodium hydroxide compensated for the dilution and fingering, increasing the recoveries for smaller slug sizes.



#### ACKNOWLEDGEMENT

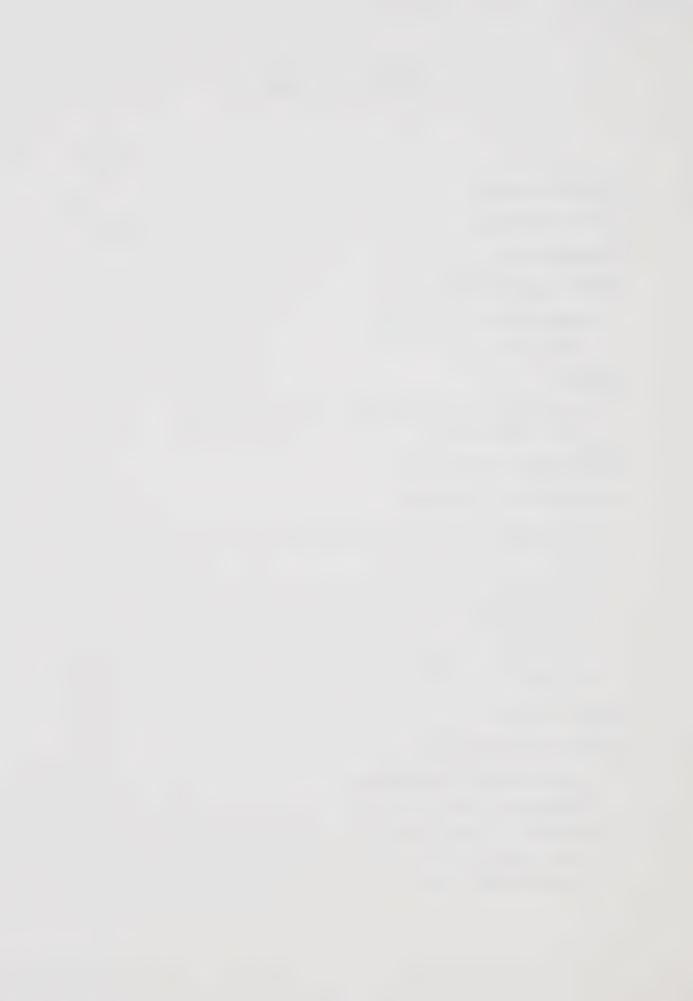
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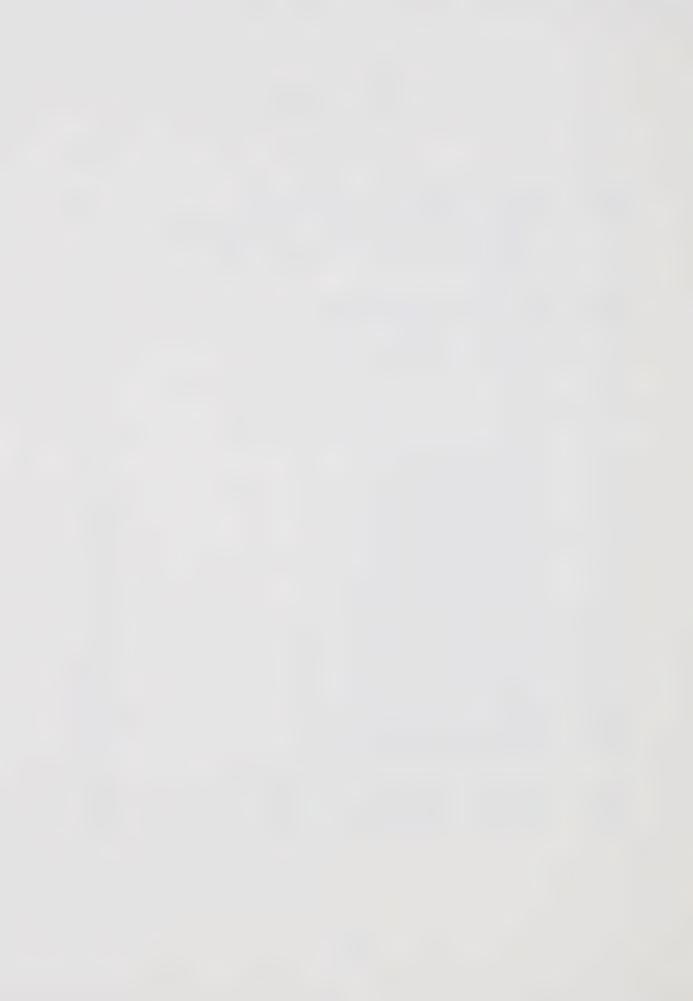
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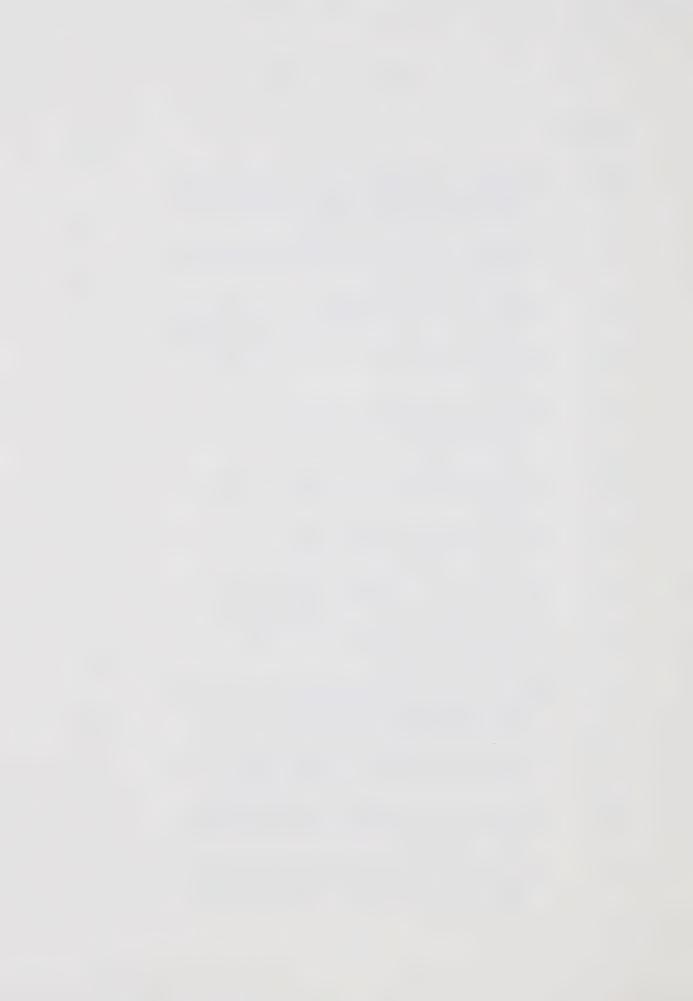
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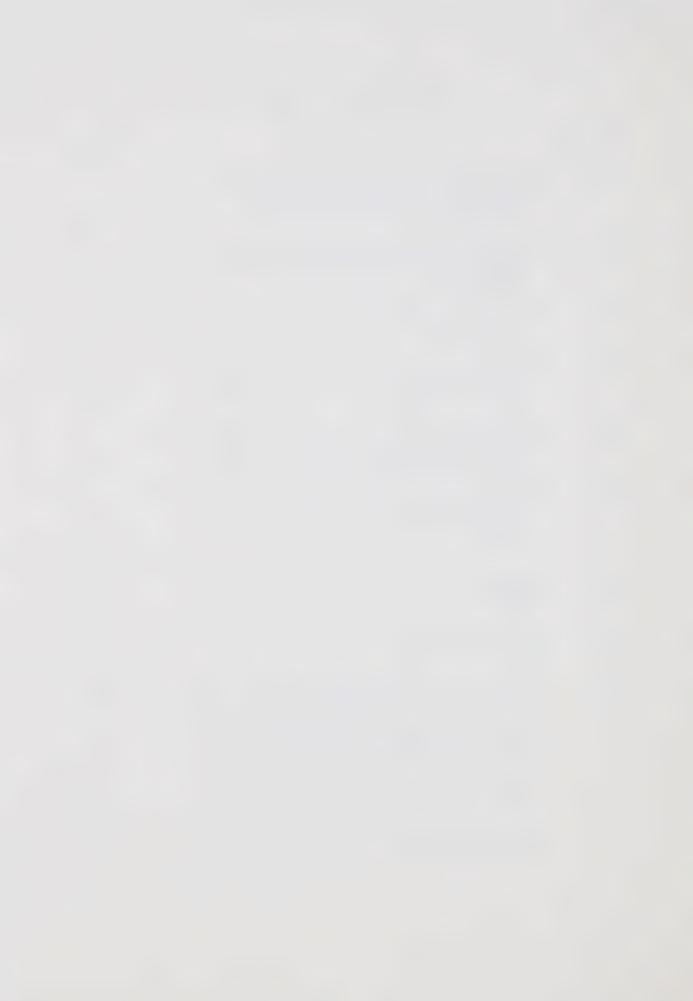
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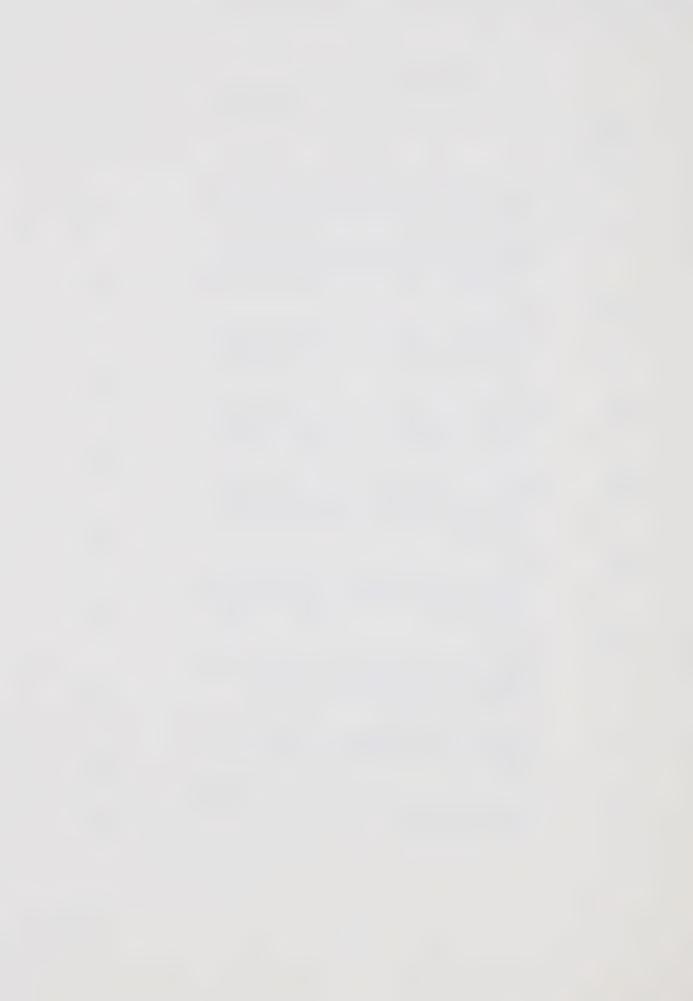
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#### INTRODUCTION

Significant reserves of heavy crude oils are located in Western Canada. Using conventional methods of recovery, these reserves can only be partially recovered. Westfall states that approximately 5 to 6 percent of the oil is recoverable by primary methods and 10 to 12 percent is recoverable by water flood. With the increasing world demand for oil an efficient economical method is required for the recovery of heavy crude oils.

Several previous studies have been conducted at the University of Alberta on methods of improving recoveries from viscous crude systems. Collins investigated the influence of viscosity ratio on the recovery efficiency of viscous crude oil in long unconsolidated sand packs using a native brine.

Scott<sup>40</sup> studied the suitability of adding different acids and bases to the water when flooding crude oil reservoirs. He found that a low concentration of sodium hydroxide would reduce water-oil interfacial tension, cause an oil-wet sand to become more water-wet and significantly increase oil recovery.

Fazil<sup>20</sup> investigated the effect of carbonated brine on the recovery of viscous crude oil. He obtained significant increases in recovery, which he attributed



to the reduction of crude oil viscosity and oil-water interfacial tension.

Scott 41 studied the effects of different chemicals on water flood recovery of viscous crude oil. He found that recovery could be significantly increased by the injection of a 0.1 percent by weight or greater concentration of sodium hydroxide in brine. He indicated that the sodium hydroxide requirements are greatly reduced if sodium chloride was added to the injection fluid.

The addition of chemicals to only a portion of the injected fluid has been investigated by several authors 30,37,43. They found that a small slug of a chemical solution, if properly designed, can achieve similar recoveries to water floods which have the chemical added to the entire injected fluid.

The purpose of this study was to investigate the effect on viscous crude oil recovery of adding sodium hydroxide to only a portion of the displacing water.

Reservoir conditions typical of the Lloydminster Sparky heavy crude oil reservoirs were duplicated where possible.



#### LITERATURE REVIEW

## Chemical Water Flooding

Early investigations of the use of chemical additives to improve water flood recovery were done by Nutting  $^{36}$  in 1923, Uren and Fahmy  $^{46}$  in 1927 and Beckstrom and Van Tuyl  $^4$  in 1927.

Nutting suggested that there was an attraction between the silica particles (SiO<sub>2</sub>) and the hydrogen ions in the water which would lead to the formation of a layer of siloxyl radicals (SiOOH) on the rock surface. The acidic siloxyl was thought to react with the basic constituents of the oil to form a stable oil layer on the rock surface. He theorized that if a strong base was added to the displacing water it would replace the weaker base (oil) siloxyl radical on the rock's surface and improve the recovery.

Beckstrom and Van Tuyl performed displacement tests on sand cores and concluded that only strong bases and weak acids were effective as water flooding additives. Uren and Fahmy confirmed this conclusion and attributed the increase in recovery to a reduction in interfacial tension between the oil and water. They suggested that there was also a reduction in interfacial tension between the water and rock due to a reaction



at the rock surface.

Bartell and Miller<sup>3</sup> found that the addition of inorganic chemical additives produced equivalent recoveries in a water-oil system and a water-benzene system although the interfacial tensions of the two systems were quite different. They concluded that recoveries were increased by altering the rock-water interface and that the altering of the oil-water interface did not have a significant effect.

Terwilliger and Yuster 45 were the first to differentiate between surface active and surface inactive agents. Surface active agents or surfactants are usually polar-nonpolar molecules which concentrate at interfaces and lower the interfacial tension. Surface inactive additives such as sodium hydroxide, sodium carbonate, and sodium sulfite do not lower the interfacial tension as much as surface active additives. The surface inactive additives advantage is that they are not adsorbed to the same extent as surface active compounds since they do not concentrate at the interfaces. Terwilliger and Yuster 45 found that a 0.1 percent by weight sodium hydroxide solution could reduce residual oil saturation in cores that were previously water flooded from 52 percent to 35 percent.

Calhoun et al. 7 conducted a series of tests on



Bradford sand cores using sodium hydroxide as an additive in the displacing water. In all cases, the residual oil saturations after flooding with water containing sodium hydroxide (0.5 percent by weight) were lower than those obtained for equivalent floods using water. The increase in recovery was attributed to a decrease of interfacial tensions and a change in wettability. The decrease of interfacial tensions was said to be caused by the formation of surface active groups as a result of the reaction of sodium hydroxide with the polar compounds in the crude oil. It was noted that the use of chemicals such as sodium hydroxide which are not surface active additives, can lower interfacial tensions without great losses due to adsorption observed when using surface active agents.

Reisberg and Doscher<sup>39</sup> conducted tests on Ventura crude oil, to find the effect of pH on the oil water interface. They found that weak sodium hydroxide solutions would displace the oil from the surface of a glass slide, whereas a weak solution of hydrochloric acid, having the same interfacial tension to oil, would displace little of the oil. This was attributed to the presence of rigid films at the oil-water interface which are stable in the presence of an acidic aqueous phase, but broke down in the presence of an alkaline aqueous phase.



The rigid film was isolated and found to be a highly oxygenated, low molecular weight constituent of the resins and asphaltenes. This was in agreement with earlier investigations 15,17,18 which suggested that porphyrins with heavy metal molecules attached were the main cause of the rigid films in asphaltic crude oils. Reisberg and Doscher 39 concluded that the reduction of interfacial tension and changes in wettability were due to a component of the oil which was initially positively adsorbed at the oil-water-solid interface. The component, when dissolved in the aqueous phase by interaction with the basic sodium hydroxide, changes the surface forces of the aqueous phase.

The increase in recovery due to the alkaline solution occurred after the breakthrough of the front. This was attributed to adsorption and reaction at the sand surface reducing the concentration of the sodium hydroxide at the flood front as it moved through the reservoir. They suggested that the increase in recovery was not due just to the reduction of the oil-water interfacial tension but also to a change in the oil-solid and water-solid interfacial tension.

Dunning and Johanson 18 found that the displacement efficiency of inorganic solutions such as those containing sodium hydroxide (builders) are dependent



upon the pH of the solutions. They attributed the reduction in interfacial tension to a chemical reaction on the sand surface that caused an irreversible adsorption of the sodium hydroxide. Dunning and Johanson 18 compared displacement efficiencies of inorganic additives with other additives and found them surpassed only by expensive nonionic surfactants.

dilute sodium hydroxide solutions to displace viscous crude (Lloydminster) in unconsolidated packs of Sparky sand. Flooding with sodium hydroxide changed the sand from a neutral or partially oil-wet state to a waterwet state and drastically lowered the interfacial tensions. Sodium hydroxide concentrations of 0.005 percent and 0.001 percent by weight produced recoveries of 50.8 and 56.2 percent of the initial oil in place respectively, compared to 39.9 percent recovered by injecting brine. Scott 40 noted that there was a delay between the time the front passes through the reservoir and the increase in recovery. He suggested that this was due to dilution and fingering preventing the sodium hydroxide from fully contacting the rock surfaces.

Scott 41 investigated the use of chemical additives to improve the water flood recovery of viscous crudes. He ran tests on Lloydminster crude in



short core packs of unconsolidated Sparky sand. Sodium hydroxide in brine solution of 0.1 percent by weight was found to result in the most efficient recoveries. A larger concentration did little to increase recovery whereas a lower concentration resulted in a decreased recovery. The presence of sodium chloride helped reduce the amount of sodium hydroxide required.

Scott 41 suggests that the displacement took place by an emulsion slug mechanism. Dilution and reaction at the leading edge of the injected chemical front lead to the formation of an emulsion which would reduce the conductivity of the flow path. The reduced conductivity in the flow path would force the water to flow through the next path of least resistance. The emulsified water would flow only when all the paths of least resistance were blocked. The emulsion would move as a front and because of its low mobility (and thus a more favorable mobility ratio) would more efficiently displace the oil.

Cooper 11 ran sodium hydroxide displacement tests on Lloydminster crude oil in Berea sandstone cores. He found that the recovery using a 0.2 percent by weight sodium hydroxide solution increased with temperature to a much greater degree than equivalent floods using distilled water. This was attributed to



the interfacial tension reduction caused by the sodium hydroxide being sensitive to temperature. Cooper correlated interfacial tension with sodium hydroxide concentration and found that it reached a minimum between 0.1 and 0.3 percent sodium hydroxide by weight. Monitoring of the effluent pH indicated that 0.1 pore volume of water was produced before the pH increased to that of the injected water. This delayed increase in pH suggests that sodium hydroxide was adsorbed in the system.

Ehrlich et al. 19 investigated the use of sodium hydroxide in light oil reservoirs to change both wettability and interfacial tension in order to increase oil recovery. They concluded that increased recovery was due to a wettability alteration. Also, they concluded that if the interfacial tension was lowered enough it would also increase recovery. They found that in a wettability alteration water flood recovery was not rate dependent but was significantly affected by how early in the water flood sodium hydroxide was injected. Initiating sodium hydroxide injection early in the life of the water flood greatly increased recoveries. When interfacial tension alteration was the primary mechanism, recovery was highly rate dependent but did not depend on the state of depletion of the reservoir when the sodium hydroxide was injected. They stated that to predict the effect of sodium hydroxide



on water flood recovery, the interfacial tension and compatability of the sodium hydroxide to the formation should be tested. Laboratory water floods of reservoir cores were also recommended.

Jennings et al. <sup>27</sup> conducted an investigation of the use of sodium hydroxide to improve water flood recovery of viscous crudes in water-wet porous media. They stated that the addition of sodium hydroxide to the flood water reduced the interfacial tension between the oil and water (sodium hydroxide reacted with the carboxylic acid in the oil to reduce interfacial tension). If the tension was lowered below 0.1 dyne/cm increased recoveries were obtained. Jennings et al. <sup>27</sup> also stated that the addition of sodium hydroxide to the water flood reduced the quantity of sodium hydroxide required but due to the larger amounts of sodium chloride required it was concluded to be uneconomical.

Jennings et al. 27 suggested that lowering the interfacial tension resulted in the formation of an emulsion that due to its lowered mobility could sweep the reservoir more efficiently than a conventional water flood. They based this theory on the fact that when oil-in-water emulsions induced by sodium hydroxide were injected into the reservoir recovery was increased significantly.



Jennings et al. <sup>27</sup> found that a 15 percent pore volume slug of 0.5 percent by weight sodium hydroxide obtained similar recoveries to the continuous injection of 0.5 percent by weight sodium hydroxide.

A field test<sup>26</sup> using sodium hydroxide in a watered out portion of the Muddy J sand of the West Harrisburg Nebraska field produced a significant amount of oil. The reservoir was oil-wet prior to the test and was changed to preferentially water-wet by the sodium hydroxide.

A field trial of the caustic flooding process was conducted on the viscous crude Whittier Field in Whittier, California. More oil was produced than would have been produced from a continuous water flood.

Caustic also appeared to improve the injectivity of the injection wells.

## Slug Flooding

Early investigators of chemical water flooding assumed that it was necessary to add the chemical additive to all of the water injected. In 1952 Preston and Calhoun 37 suggested that only a part of the injected water be treated. It was suggested that an injected slug of surfactant solution would form a narrow band



which could be pushed through the reservoir by untreated water. As the band of surfactant or chemically treated water passed through the reservoir it would release the oil from the rock and drive the oil ahead of it. They stated that movement of the surfactant slug through the reservoir could be described by the application of the theory of chromatography, although they presented no experimental evidence to support this mechanism.

Chromatography is a technique used to separate components in a mixture by utilizing the selective adsorption phenomenon of a porous medium. When a solution of concentration Co flows through a porous medium, the solute is adsorbed and the solvent moves ahead at a higher velocity. The solute remains in the solution only where porous surfaces are saturated with solute. This causes an adsorption zone which progresses through the porous medium at a slower velocity than the solvent. When pure solvent is injected behind the slug a trailing mixing zone develops, separating the pure solvent from the slug.

The shape of the advancing concentration profile is determined by the kinetics of adsorption. If the adsorption equilibrium occurs at a finite rate, both leading and trailing edges are diffuse. The size of the slug zone increases and the concentration



decreases as it progresses through the reservoir (see Figure 1-1).

If the adsorption equilibrium is instantaneous, the concentration profile depends upon the shape of the adsorption isotherm as illustrated in Figure 1-2. The adsorption isotherm is the equilibrium relationship between the amount of solute adsorbed and the amount in the solution. One procedure to obtain the adsorption isotherm, described by Preston and Calhoun 37, is to establish a known concentration in a solution and the difference in concentration of the solute before and after it contacted the porous media would be the amount adsorbed by the porous media. If this procedure is followed several times with different concentrations of solute an adsorption curve can be constructed.

Preston and Calhoun <sup>37</sup> rearranged DeVault's <sup>14</sup> basic equations of chromatography to obtain equations 1-1, 1-2 and 1-3, which describe the position of the leading edge of the slug, position of the trailing edge of the slug and the minimum effective slug size.

$$x_{d} = \frac{V_{t}}{A\emptyset} \frac{1}{1 + \left(\frac{1-\emptyset}{\emptyset}\right) \circ \left(\frac{f(C_{0})}{C_{0}}\right)}$$
1-1



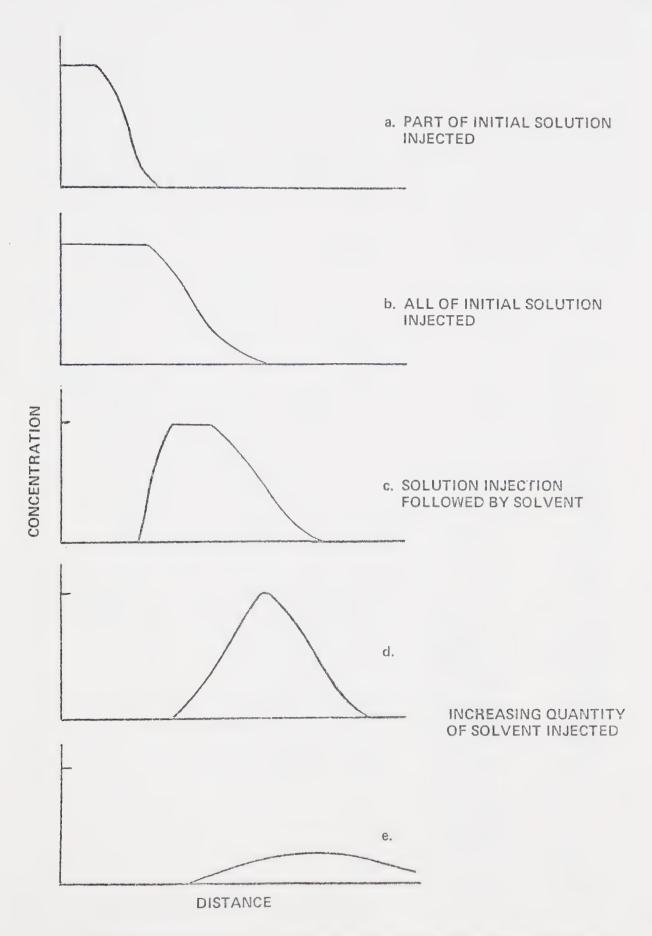
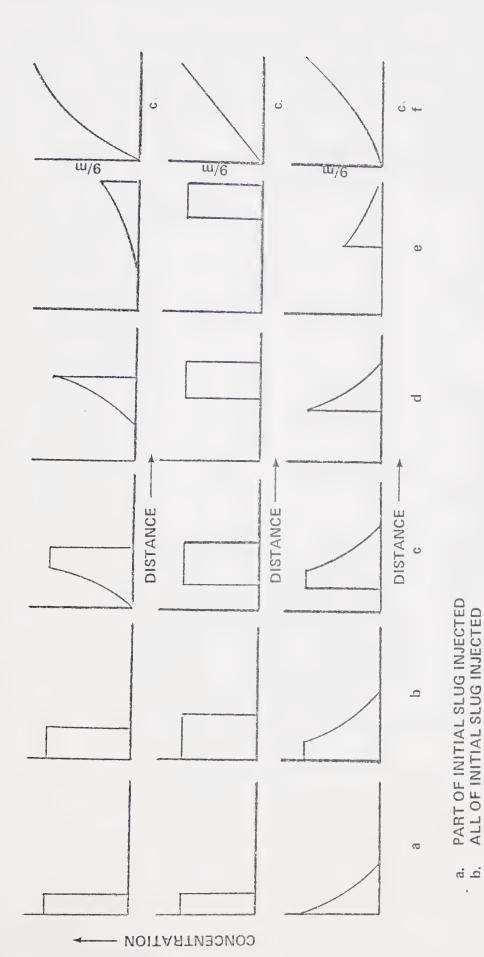


FIGURE 1-1 SCHEMATIC REPRESENTATION OF THE MOVEMENT OF AN NON-INSTANTANEOUS EQUILIBRIUM ADSORPTION ZONE



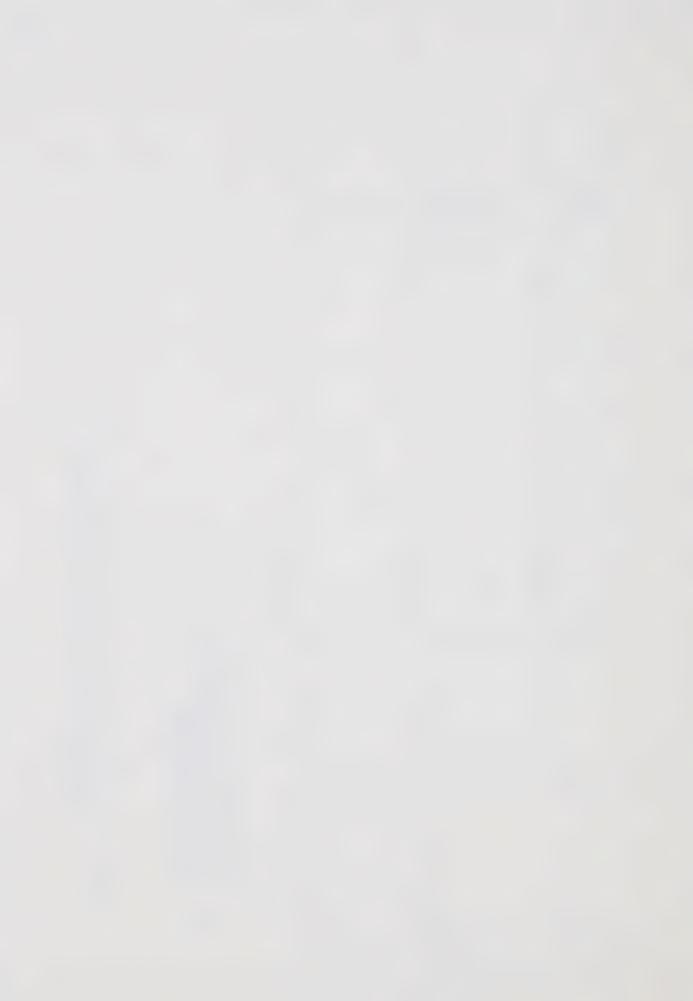


SCHEMATIC REPRESENTATION OF THE MOVEMENT OF AN INSTANTANEOUS EQUILIBRIUM ADSORPTION ZONE FIGURE 1-2

INCREASING VOLUME OF SOLVENT INJECTED

ADSORPTION ISOTHERM

c, d, e. f.



$$X = \frac{V_{S}}{A\emptyset} \left[ \frac{1}{1 + \left(\frac{1-\emptyset}{\emptyset}\right)\rho \ f'(C)} \right]$$
 1-2

$$V_{m} = X_{dt} A \varnothing P \left[ \frac{f(C_{o})}{C_{o}} - f'(C_{o}) \right]$$
 1-3

Where:

 $X_{
m d}$  = distance from injection source to the leading edge of the solution zone, cm,

X = distance to trailing edge of slug from injection source, cm,

 $X_{dt}$  = total length of adsorbant column, cm,

 $V_t$  = volume of fluids injected ( $V_t = V_s + V_t$ ) volume of displacing fluid), cc,

 $V_s$  = volume of solvent injected, cc,

 $V_{m}$  = minimum effective slug size, cc,

A = cross sectional area,  $cm^2$ ,

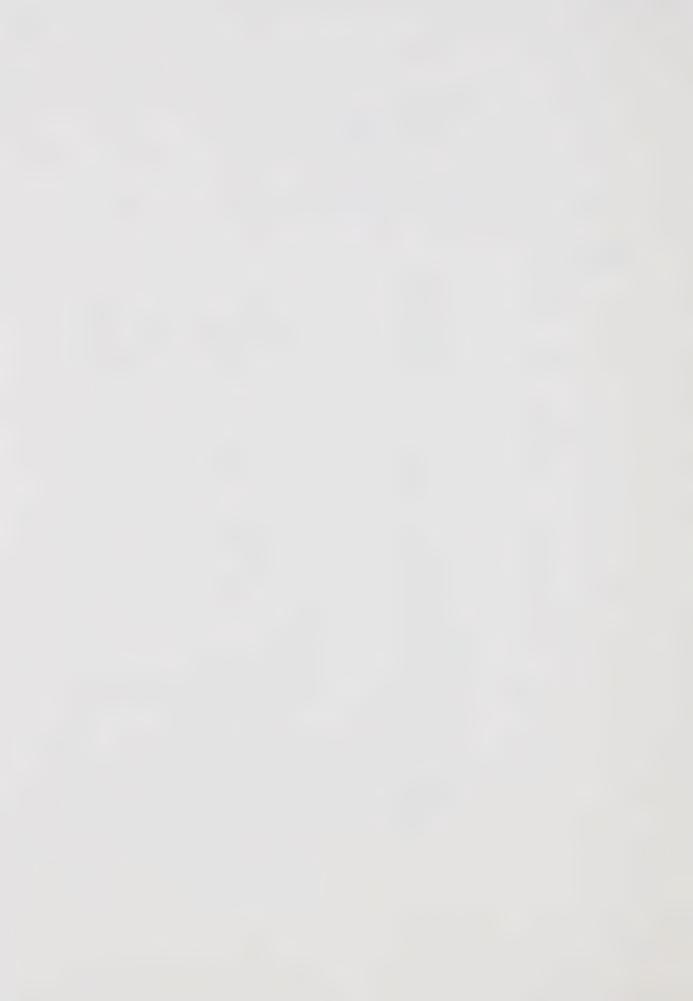
Ø = porosity, fraction,

 $\rho$  = density of adsorbant, gm/cc,

f(C<sub>o</sub>) = function notation for general adsorption isotherm,

 $f'(C_0) = first derivitive of the general adsorption isotherm,$ 

 $P = \rho (1-\emptyset)/\emptyset .$ 



Johnson<sup>30</sup> stated that two assumptions were implicit in the suggestion that a slug could perform as well as continuous injection. First, the time required for the surface active agent to release the oil from any point in the reservoir was less than the time it took for the surfactant bank to pass that point. Second, the released oil must travel faster than the surfactant bank. Johnson<sup>30</sup> stated that the second assumption is probably valid. Partially adsorbed surfactant moves much slower than the water eluting it. Thus, the oil would be banked ahead of the water with the solute removed, which in turn moves ahead of the surfactant slug.

Johnson 30 extended DeVault's 14 basic equation to obtain an equation for minimum effective slug size

$$V_{\min} = f(C_0)/C_0 - f(C_0)$$
 1-4

He evaluated the adsorption isotherm by the expression

$$f(C_0) = (N-1)C_0$$
 1-5

Where: N = number of pore volumes injected until the surfactant breaks through.

Johnson 30 concluded that the best results were



obtained when the surfactant was injected early in the life of the reservoir.

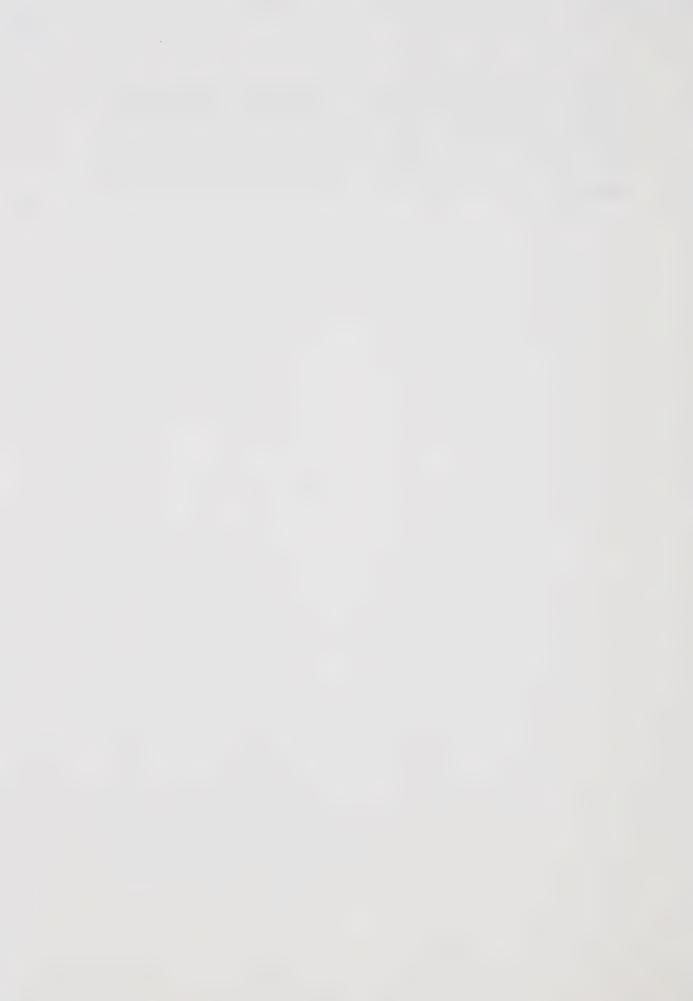
Taber 43,44 pointed out that the chromatographic theory used by Preston and Calhoun 37 assumed that a portion of the slug was full strength until breakthrough. This requires the injection of large quantities of surfactant to account for adsorption and dilution losses.

Taber 43,44 ran displacement tests at various concentrations which seemed to confirm his theory. He also found that adsorption losses increased with concentrations less than 1000 ppm when using Triton X-100 on Berea sandstone. At concentrations of Triton X-100 greater than 1000 ppm adsorption was insensitive to concentration.

Since slug concentration is directly proportional to the rate of movement of the slug through the reservoir, Taber postulated that a small, high concentration slug would achieve the same results as a large, low concentration slug. This would lead to a rapidly moving slug near the injection well that would move more slowly as its concentration decreased. The rapid movement of the slug through the reservoir results in less dispersion, reducing the amount of water required to push the slug through the reservoir. Moore and Blum 34 stated that a high concentration slug is more effective because it



causes a sharp reduction of interfacial tension which is more effective in displacing the oil than a gradual reduction of the interfacial tension typical of dilute solutions.



## THEORY

## Interfacial Tension, Adhesion, Wettability, and Adsorption

Surface activity in a reservoir is dependent upon the interfacial tension between fluids, and adhesion between the rock and the fluids. Interfacial tension and adhesion are force summations of the interaction of the molecules of two different materials across their interface.

The universal attraction between all molecules is fundamental to all aspects of surface activity.

Garrett<sup>22</sup> states that all forces between molecules are electrostatic consisting of van der Waal's force of attraction and the Coulombic energy of attraction between ions. An interface is formed between the water and oil because the force of attraction between the water molecules is stronger than the oil-water molecular attraction. This is due to the water molecules being polar and similar in size, whereas the oil molecules vary in size and are generally non-polar. Thus, if an oil molecule becomes immersed among water molecules, it will be expelled since it blocks the attraction between the water molecules.



Miscibility of some hydrocarbon compounds in water is caused by their structural polarity. Some hydrocarbon compounds have attractive forces similar to those of water allowing contact between the individual water and oil molecules. The imbalance between the attractive forces of the water and oil molecules leads to an imbalance of forces at the interface. This is corrected by the contraction of one fluid and the expansion of the other until the forces are balanced. Usually the fluid with the stronger intermolecular attraction will contract, and reduce the area of the interface. The surface energy in each fluid required to form the interface is called the interfacial tension. Antanouv's rule (Equation 2-1) states that interfacial tension is equal to the differences between the surface tensions of the fluids. (Surface tension is equivalent to the fluid-air interfacial tension).

$$\Gamma_{\text{ow}} = \Gamma_{\text{aw}} - \Gamma_{\text{ao}}$$
 2-1

where:

r<sub>ow</sub> = interfacial tension between oil and
 water, dyne/cm,

 $\Gamma_{ao}$  = surface tension between air and oil, dyne/cm.



Since the interaction between the two liquid phases takes place on the surface of the rock, the forces between the fluids and the rock (adhesion) must also be considered.

Dupre's equation describes the interaction between the fluid and the solid terms of their interfacial tensions.

$$W_{a} = \Gamma_{sa} + \Gamma_{la} - \Gamma_{sl}$$
 2-2

where:

 $W_a = \text{the work of adhesion, erg/cm}^2$ ,

 $\Gamma_{sa}$  = interfacial tension between solid and air, dyne/cm,

Γ<sub>la</sub> = interfacial tension between liquid and air, dyne/cm, and

 $\Gamma_{sl}$  = interfacial tension between solid and liquid, dyne/cm.

Young developed a more practical equation which describes the work of adhesion in terms of liquid-air interfacial tension and the contact angle.

$$W_{a} = \Gamma(1 + \cos \theta)$$
 2-3

where:

 $W_a = \text{the work of adhesion, erg/cm}^2$ ,

 $\theta$  = contact angle, and

Γ = surface tension of the liquid, dyne/cm.

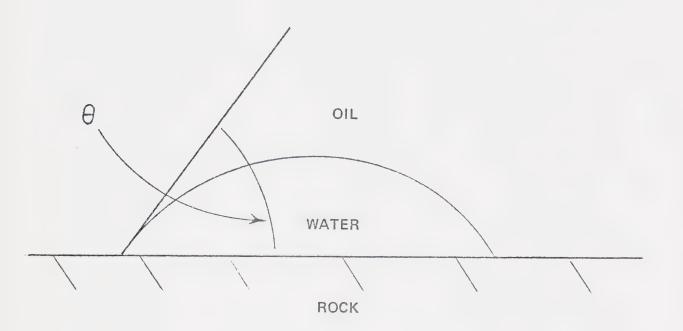


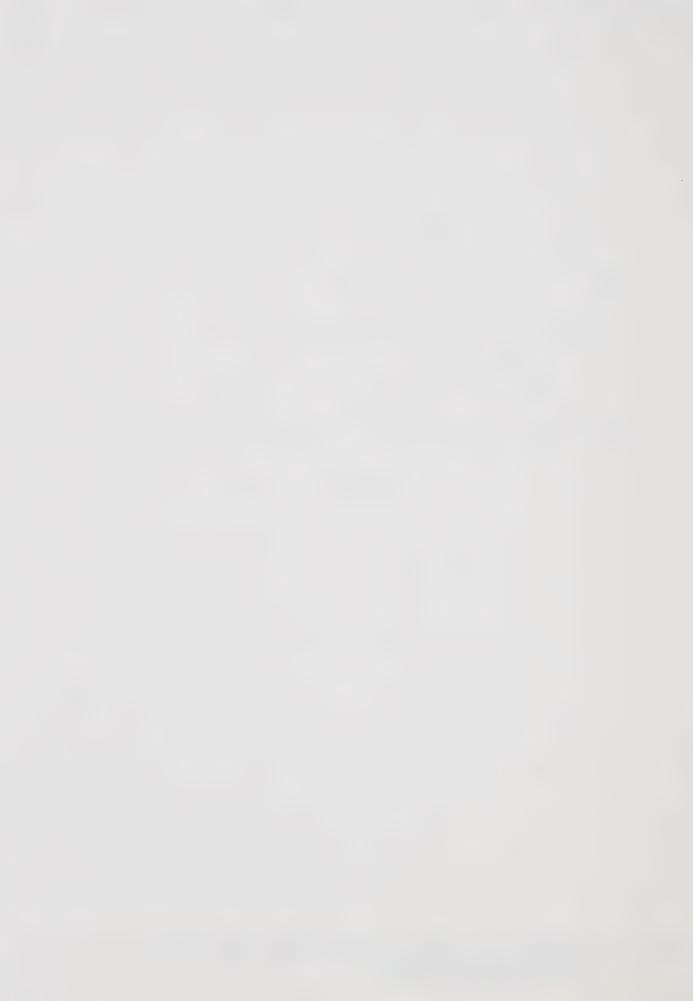
The contact angle is the angle of intersection between the two fluids at the rock surface, measured through the denser phase. (See Figure 2-1). Thus, by measuring the surface tension of the fluids and the contact angle, a value for the work of adhesion can be obtained. By combining the interfacial forces between the oil and the water with the oil-rock and water-rock work of adhesion, an equilibrium or summation of the forces at the interface is obtained.

Generally, wetting is defined as the phenomenum that occurs when a solid and a liquid phase come in contact in such a manner as to form a solid-liquid interface. In reservoir engineering, "wetting" or "preferential wetting" is used to describe the property of the rock that allows the wetting fluid to spread over the rock surface in the presence of another fluid.

Reservoir rocks are considered either oil-wet, water-wet or intermediately wet.







interfacial tension with the other fluid.

A surfactant is a surface active chemical which concentrates at an interface and upsets the equilibrium of the interfacial forces. The surfactant molecule is highly symmetrical, one portion being polar and the other, non-polar. In an oil-water system, the polar section is attracted by the polar water molecules, while the non-polar section is attracted by the non-polar oil. Thus, the surfactant molecule migrates to the oil-water interface (Gibb's rule of solution concentration at an interface) and positions itself so that its polar section is in the water, while the non-polar section is in the oil. This surfactant film lowers the amount of energy required to maintain the interface, thereby reducing interfacial tension.

The removal of oil from the surface by the use of a surfactant occurs in one or both of two mechanisms:

- 1. Solubilization
- 2. Surface Roll-up

Solubilization is the process by which the oil molecules are surrounded by the surfactant, forming micelles in the aqueous phase. A micelle is a structure formed by an oil molecule surrounded by surfactant molecules in such a way that the non-polar portion of the surfactant is towards the oil and the polar portion is towards the



water. This allows the oil molecule to be removed into the aqueous phase.

Surface roll-up is a mechanism where the surfactant is adsorbed by the solid surface and forms a monolayer
upon it. This reduces the surface tension of the
aqueous phase, and the amount of water required to
adhere to the surface. To balance this reduction in
surface forces, the contact angle must also become less.

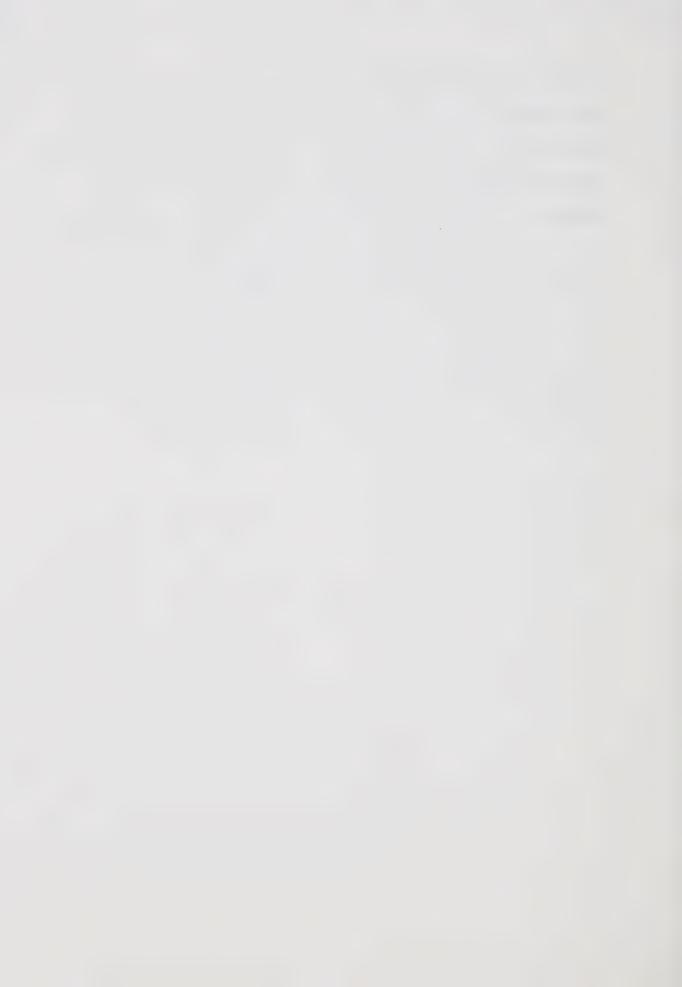
If the surface tension and work of adhesion of the
aqueous phase is lowered enough, the aqueous phase will
displace the oil from the surface.

In general, adsorption is the physical and chemical process by which one phase interacts on a molecular scale with another phase, to reduce the energy of their interface. In this study, only the highly specific adsorption between a solid or liquid and a solution will be discussed. Irreversible adsorption occurs when a component of one phase reacts with a component of the other phase to form a reaction product at the interface.

Reversible adsorption occurs when surface energy at an interface is lowered by the attraction of a high concentration of solute molecules to the surface of the solution. Gibbs 24 showed that an increase in solute concentration at the interface must occur to reduce the



surface to its lowest energy state. The presence of the solute molecules causes a disruption of the bonding between the solvent molecules. Adsorption of the solute on the interface is dependent upon the chemical and physical structures of the solute, solvent, and adsorbent. When the two phases are similar, the interface is at a low energy level and requires little adsorption to lower it further. Highly dissimilar phases result in a high degree of adsorption, because of their high energy interfaces. The most effective tension-lowering solutes are the previously mentioned surfactants.



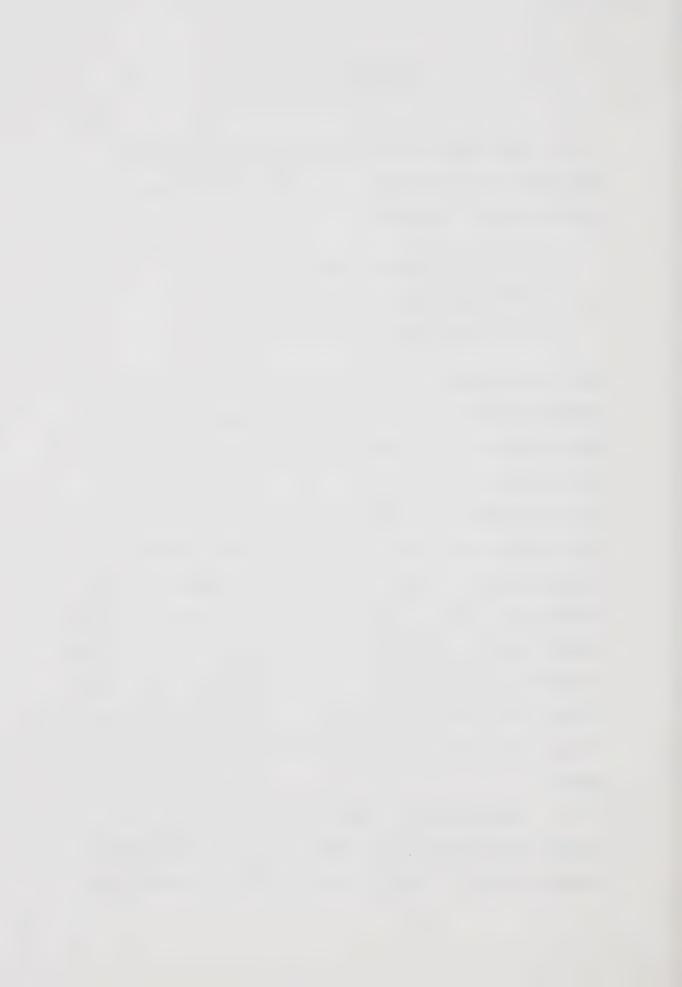
#### EXPERIMENTAL EQUIPMENT

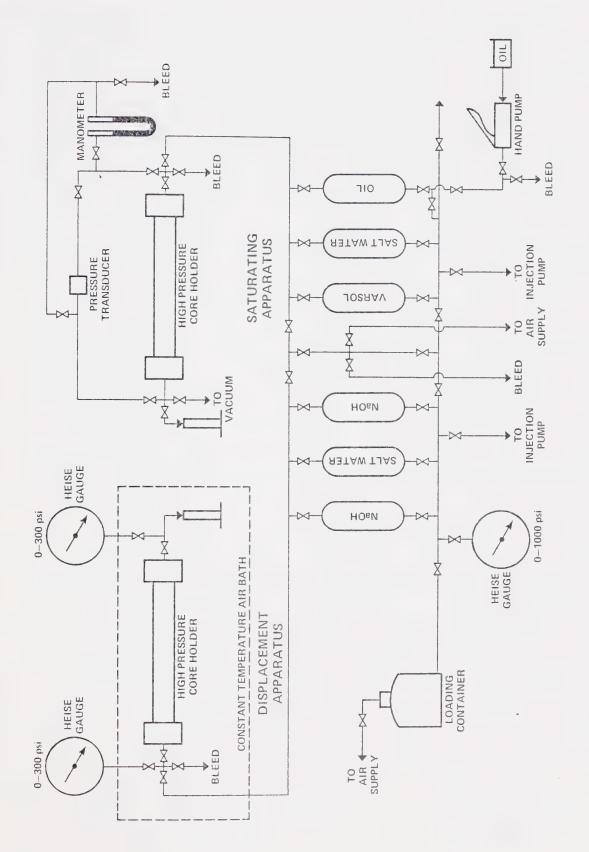
The displacement and saturating apparatus schematically diagrammed in Figure 3-1 consists of three separate sections:

- 1. The displacement apparatus.
- 2. The saturating apparatus.
- 3. The injection cylinder panel.

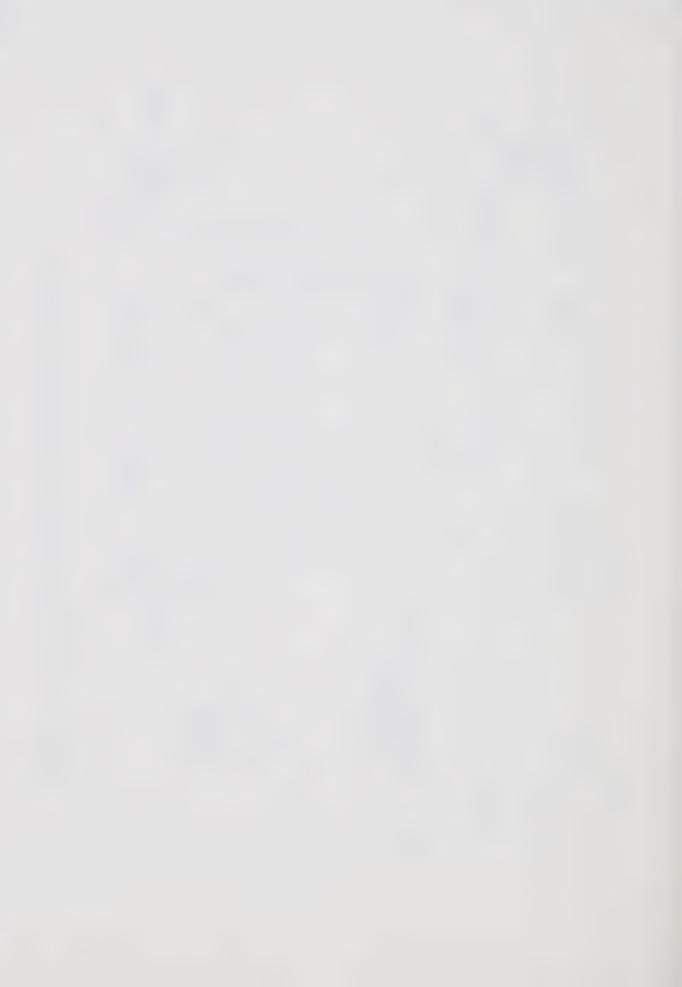
The cylinder panel consists of six 3000 cc highpressure stainless steel cylinders connected such that
mercury could be injected into the bottom of the cylinders displacing the stored fluid into either the displacing or the saturating apparatus. By isolating onehalf of the panel from the other, it was possible to
saturate one core while conducting displacement tests
on the other core. Due to the high viscosity of Lloydminster crude, it was necessary to use a hydraulic pump
to inject it into the oil storage cylinder. All lines
through which oil was passed were 1/4 inch stainless steel
tubing; all other lines were 1/8 inch stainless steel

The saturating apparatus consists of a core holder with pressure taps mounted at the upstream and downstream ends. Both a manometer and a differential





SCHEMATIC DIAGRAM OF THE EXPERIMENTAL EQUIPMENT FIGURE 3-1

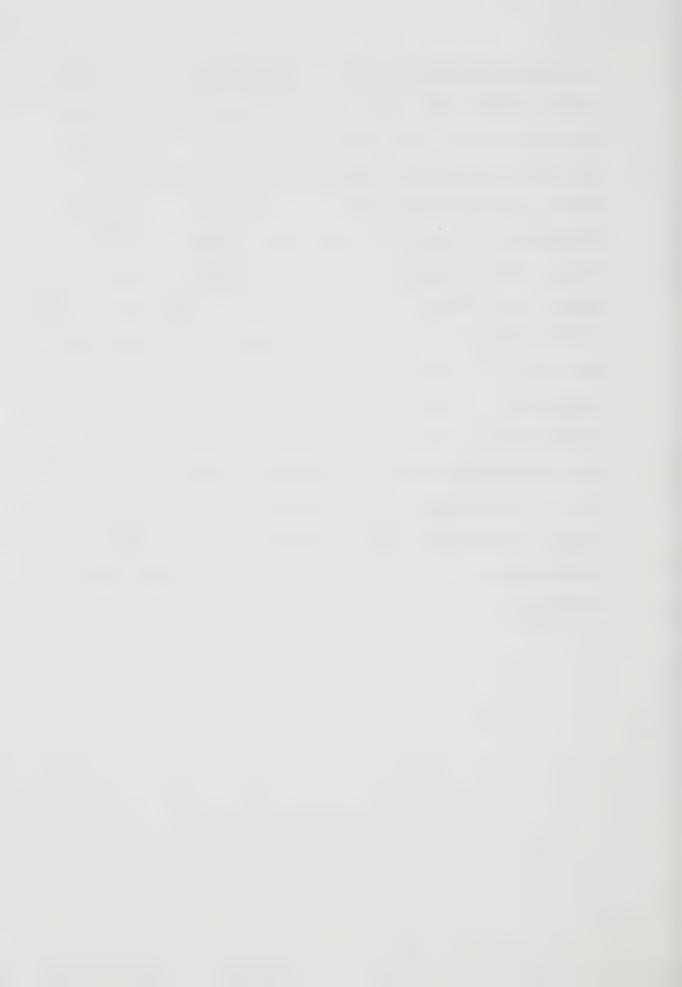


pressure transducer were used to measure differential pressure. A Validyne pressure transducer, with an accuracy of ± 0.025 psi over a range of 5 psi was used. It was bridged with a Validyne model CD15 potentiometer and read-out on an Advance Digital multimeter. Prior to each core saturation the transducer was calibrated with the manometer. A vacuum pump, connected to the downstream end of the core holder, was used to evacuate the core prior to saturation. The "Displacement" apparatus consists of the core holder with pressure taps mounted at the upstream and downstream ends. Pressure taps were connected to calibrated Heise gauges to measure the upstream and downstream pressures. displacement apparatus was enclosed in a constant temperature air bath, thermostatically controlled to within ± 1.0° F.

Two high-pressure stainless steel core holders were used. Each consisted of a stainless steel tube (97.47 cm long, 4.95 cm inside diameter) with two removable end plates. The end plates fitted over a 200 mesh stainless steel screen which prevented movement of the sand and plugging of the inlet or outlet lines. A Ruska, constant-rate, two-barrel, mercury-injected pump was used to inject mercury into the cylinders. The injection rate could be varied from 2.5 cc/hr to a maximum of 1120 cc/hr using both barrels. The effluent



from the saturating and displacement runs was collected in 50 cc centrifuge tubes. An International centrifuge was used to break the emulsions produced. The viscosity measurements were taken with a Cannon-Fenske viscometer (for opaque liquids) in a constant-temperature water bath. Wettability measurements were conducted with apparatus similar to that described by Bobek, Mattax, and Denekas<sup>6</sup>. A Lucite cell (2-inch long, 1-inch inside diameter) was used to hold the unconsolidated sand pack. A Cenco du Nouy tensiometer with a platinum ring 6 cm in circumference was used for all interfacial tension measurements. All tests at elevated temperatures were conducted in the constant temperature air bath. A Rediameter Titrator pH meter with glass electrodes was used for all pH readings. The pH meter was calibrated with a buffer solution standard after each measurement.



#### EXPERIMENTAL PROCEDURE

# Source and Handling of Materials

Two types of sand were used in this study. A Golpher sand for the 1000 series runs to establish model scaling properties and a natural Sparky sand from the Lloydminster Area for all other runs.

The Sparky sand used was obtained from a lease storage tank, having been produced along with the crude. The sand was washed with Varsol until no traces of oil were observed. It was then suspended upon a series of screens and N-Pentane was allowed to permeate through until all discoloration of the effluent N-Pentane disappeared. The sand was then dried in an oven for 5 to 12 hours at a temperature of 210° F. A considerable amount of large rust flakes were removed from the sand by passing the sand through a series of sieves. All sand particles smaller than 200 mesh were collected and removed before use.

The Golpher sand, a clean commercial sand, similar to Ottawa sand was used without alteration other than the sieve removal of particles smaller than 200 mesh.

Lloydminster crude oil treated only for removal



of water was used for all displacement tests presented in this study. An A.S.T.M. standard test for water in petroleum by distillation (A.S.T.M. designation D95-62) indicated that the oil contained 0.18 percent by volume BS&W. The crude oil gravity was found to be 16.1° API by the hydrometer method (A.S.T.M. designation D287-55). Viscosity of the crude oil was measured at several temperatures using a Cannon-Fenske viscometer for opaque liquids following the procedure outlined by A.S.T.M. test D4445-60. These properties are summarized in Appendix A.

An artificial brine was used in all the oil displacement tests. The brine consisted of 88.84 grams of sodium chloride per litre of distilled water. This was the same as the brine used by Scott 40 and Scott 41. It was selected to match the chloride ion concentration of the natural field water. Reagent grade sodium chloride was used in all brine solutions. As it was pure, it did not affect the pH of the distilled water. Commercial grade salt when added to the distilled water changed the pH from 7.6 to 9.4. Since the pH of the effluent from displacement tests was monitored, the use of commercial salt would be impractical. (Displacement tests using commercial salt showed a marked increase in recovery over tests using reagent grade salt).



### Core Packing

The core holder with the bottom end plate in position (200 mesh screen in place) was placed in a vertical position. Three electric vibrators were strapped in place, one at the top, one at the base and one at the center of the core holder. The core holder was then filled half-full of water and the vibrators turned on. The dry sand was poured into the core holder through a funnel which regulated the input to approximately 50 cc per minute until it became full. The water level was kept above the sand level in the core holder at all times. Once the core holder was full, it was tapped repeatedly using a small hammer until the sand ceased to compact. The core holder was then filled to the top with sand and the other end plate (with 200 mesh screen) attached. With the vibrators operating, water was run through the core until no more compaction occurred. each inspection for compaction the core was tapped and filled to the top with sand. When no more compaction occurred, dry air was passed through the core for 8 to 12 hours to remove the water. The core holder, full of dry sand, was then ready for the displacement test. Silica grease was used on the end plate threads to prevent any fluid loss. The end plates were tightened until the core holder was the same length for all runs.



### Measurement of Core Properties

The porosity of the sand packs were measured by the material balance method. Vacuum was drawn on the core by the pump connected to the outlet end. Brine was then injected and the injection pressure monitored until an increase was observed. The outlet end of the core holder was opened and the effluent brine collected in a graduated cylinder. Brine was flowed through the core until steady state flow conditions occurred. The pore volume of the core was taken to be the difference between the amount of brine injected and the amount of brine produced from the downstream end. Knowing the volume of the core holder, the porosity was calculated.

The absolute permeability of the sand pack was obtained by flowing brine through the core at several constant rates and measuring the differential pressure across the core. Darcy's linear flow equation was used to calculate the permeability.

After the permeability was measured, the crude oil was injected into the core and the effluent brine was measured in graduated cylinders. After breakthrough of the oil, the effluent was collected in centrifuge tubes, heated and centrifuged to break the oil water emulsion. When all traces of water disappeared from



the effluent stream, the core was ready for the displacement test. Initial water saturations and initial oil in place were obtained by maintaining a material balance on the core during the whole procedure.

# Displacement Test Procedure

After saturation and measurement of initial properties, the sand pack was placed in the constant temperature air bath and allowed to acclimatize for 8 to 12 hours. The displacement test was then run and the produced effluent was collected in 50 ml centrifuge tubes. The differential pressure across the core at the end of each sampling was tabulated along with the total volume of the effluent sample. The sample was heated and centrifuged to break the oil water emulsion, and the oil and water volumes were tabulated. For displacement tests requiring pH measurements, the effluent water, after separation, was pipetted into a 50 ml beaker and measured.

# Core Handling

Five 1000 series displacement runs were made on the same Golpher sand pack. At the conclusion of each run, the core was displaced to its residual water saturation by running crude oil through until there was



no trace of water in the effluent. Runs 2003 and 2004 were run on the same Sparky sand pack, using the same resaturation technique. All other runs were made on fresh sand packs.

## Interfacial Tension Measurement Procedure

Interfacial and surface tensions were measured using a Du Noüy ring tensiometer. The procedure outlined by A.S.T.M. test D971-50 was followed throughout. All surface tensions were measured at room temperature (76°F). All crude oil and sodium hydroxide solution interfacial tensions were measured at 87°F in the air bath. Accurate measurement of tension values less than 0.5 dyne/cm were impossible due to the high viscosity of the oil. (Unable to observe an exact break point.)

# Wettability Measurement Procedure

Two methods of measuring wettability were used.

- 1. A bench test.
- 2. The cell imbibition test.

The bench test consists of placing a drop of fluid on a dry surface and observing the rate of movement into the



sand surface and observing the rate of movement into the sand with a magnifying glass. If the fluid moved quickly into the sand, the sand was said to be wetted by that fluid. This test procedure gives a highly qualitative measurement of wettability.

The cell imbibition tests followed procedures described by Bobek, Mattax, and Denekas 6. A small lucite imbibition cell was packed with sand by vibrating the cell until the sand ceased to compact. end plate with a 200 mesh screen was then fastened on, and the packed cell weighted. The cell was saturated by evacuating it in a vacuum cell, which was then filled with saturating fluid until the imbibition cell was immersed. The imbibition cell was then re-weighed to obtain the porosity of the sand pack by weight difference. The saturated cell was then placed in the imbibition column which was filled to the graduated portion of the column, completely immersing the imbibition cell with imbibing fluid. The saturating fluid displaced by the imbibing fluid was collected and measured in the graduated portion of the column. measured displaced fluid was then tabulated along with imbibition time. All tests were run at room temperature.



#### MODEL SCALING

The use of laboratory models to predict performance of actual reservoirs requires that the physical properties of the models are scaled. If the models are properly scaled, viscous fingering and capillary end effects can be minimized or eliminated. Investigation of these scaling problems has resulted in the development of scaling groups by several authors.

Rapoport and Leas<sup>38</sup> used the following scaling factor to study capillary end effects.

 $LV\mu_{tr}$  5-1

where: L = length of the core, cm,

 $\mu_{\mathbf{w}}$  = injection water viscosity, cp.

They found that for values greater than 1.0, recovery did not change with changes in magnitude of the scaling factor. This would indicate that for systems having scaling factors greater than 1.0, capillary end effects are negligible. de Haan 13 elaborated on the Rapoport and Leas' factor to account for interfacial tension and permeability. de Haan 13 proposed the following scaling factor.



$$I = \frac{V\mu_{W}L}{\gamma\sqrt{\kappa}}$$
 5-2

where: I = de Haan scaling coefficient,

 $\mu_{\rm w}$  = viscosity of the injected water, cp,

L = length of core, cm,

 $\gamma$  = interfacial tension, dyne/cm, and

K = absolute permeability, md.

He stated that for oil-wet or neutral systems there would be no viscous fingering for scaling coefficient values less than 0.1. (The advance of one portion of the flood front ahead of the rest of the front in a homogeneous media due to viscosity differences between the displaced and the displacing fluid is called viscous fingering).

Chuoke, van Meurs and van der Poel<sup>8</sup> also developed a scaling factor to test for viscous fingering.

$$\frac{\lambda_{cr}}{h} = C \frac{3\sigma_{wo}K}{V(\mu_{o} - \mu_{w})}$$
 5-3



where:

 $\lambda_{cr}$  = critical fingering distance, cm,

o = interfacial tension, dyne/cm

K = absolute permeability, cm<sup>2</sup>,

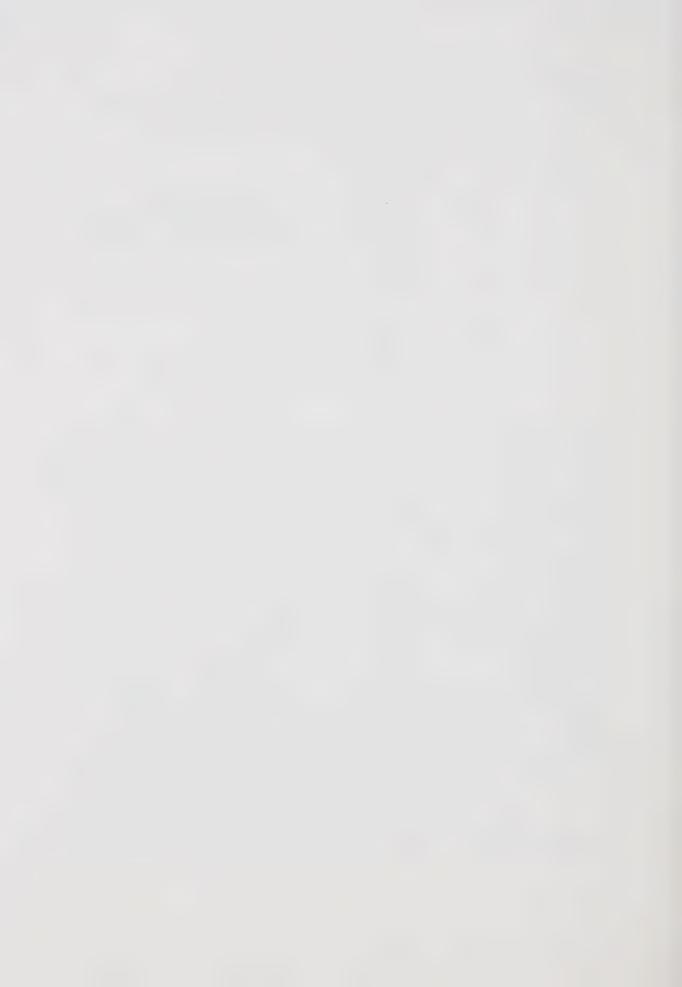
 $\mu_0$  = oil viscosity, poise,

 $\mu_{w}$  = water viscosity, poise, and

h = lateral dimension of core, cm.

They showed that for scaling factor values greater than 1.0 fingering did not occur since the mean thicknesses of the fingers were larger than the diameter of the core. For a scaling factor in the region of 1.0, prolific viscous fingering occurs. If the scaling factor values are much less than 1.0 minute fingers occur with a mean thickness so small that the recoveries are insensitive to fingering. As illustrated in Figure 5-1 recovery is sensitive to changes in the scaling factor for scaling values approaching 1.0. Recovery changes little when the scaling factor is much greater or much less than 1.0.

For the core system used in this study a series of displacement tests at different injection rates were



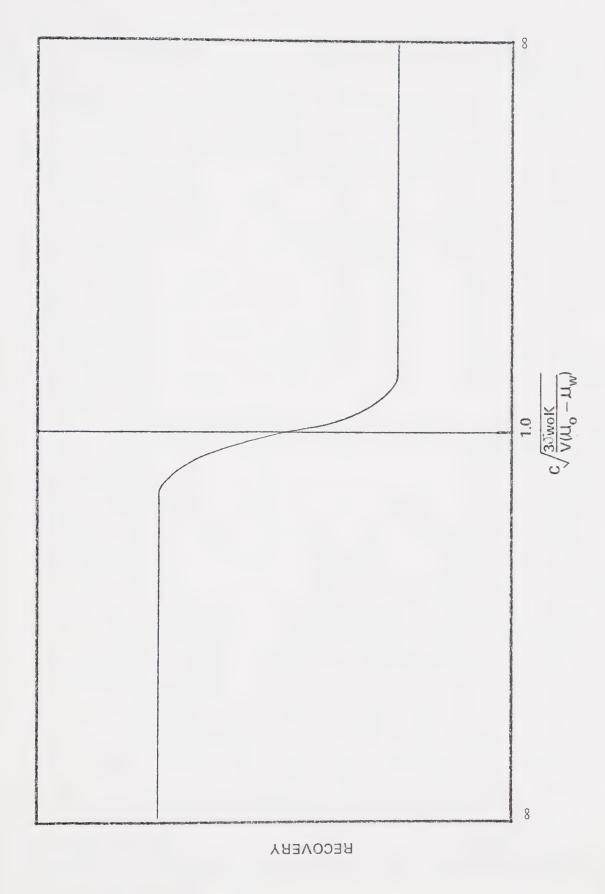


FIGURE 5-1 IDEALIZED DIAGRAM OF RECOVERY AS A FUNCTION OF CHUOKE ET AL. SCALING COEFFICIENT



run. A summary of displacement test initial properties and recoveries is presented in Table B-1. Also included in Table B-1 are the values of the Rapoport and Leas, de Haan, and Chuoke et al. scaling coefficients for the core system at each rate.

The Rapoport and Leas scaling coefficient was plotted as a function of the injection rates used in this study (Figure 5-2). A rate greater than 11.5 cc/hr was required to negate capillary end effects. (A rate greater than 11.5 cc/hr is required to produce a scaling factor value greater than 1.0).

The de Haan and Chuoke et al. scaling coefficients were plotted as a function of recovery in Figures 5-3 and 5-4 respectively. To obtain the Chuoke et al. coefficient a value of 250 was used as the dimensionless coefficient. This value was suggested by Collins for viscous crude systems with initial water saturations.

Except for a small decrease in the breakthrough recovery versus the Chuoke et al. coefficient and a small increase in the breakthrough recovery versus the de Haan coefficient, recovery showed no sensitivity to the magnitude of either scaling coefficient. The differences between the breakthrough curves were attributed to experimental error. It was difficult to obtain a precise breakthrough due to the severe emulsification of the water in the oil.



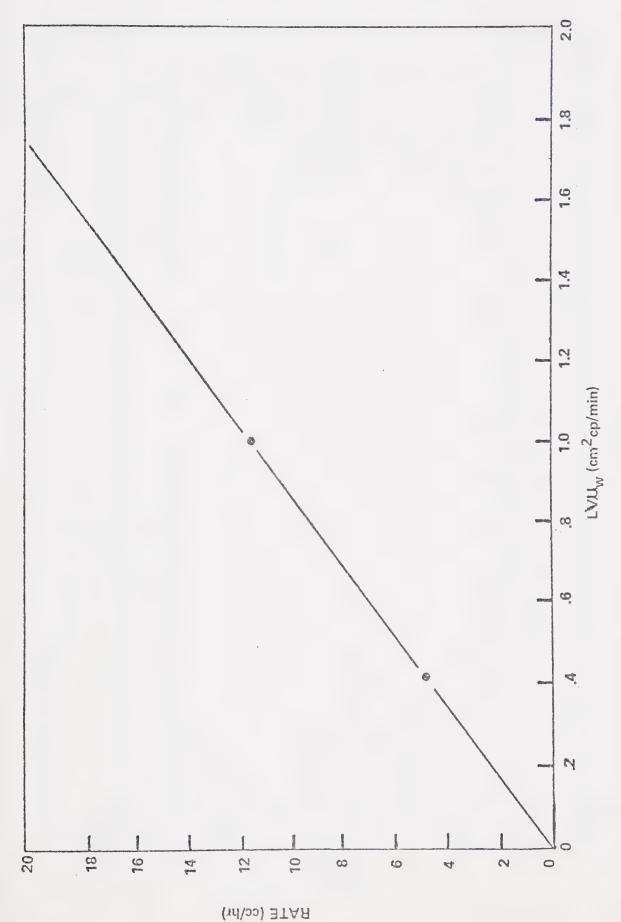
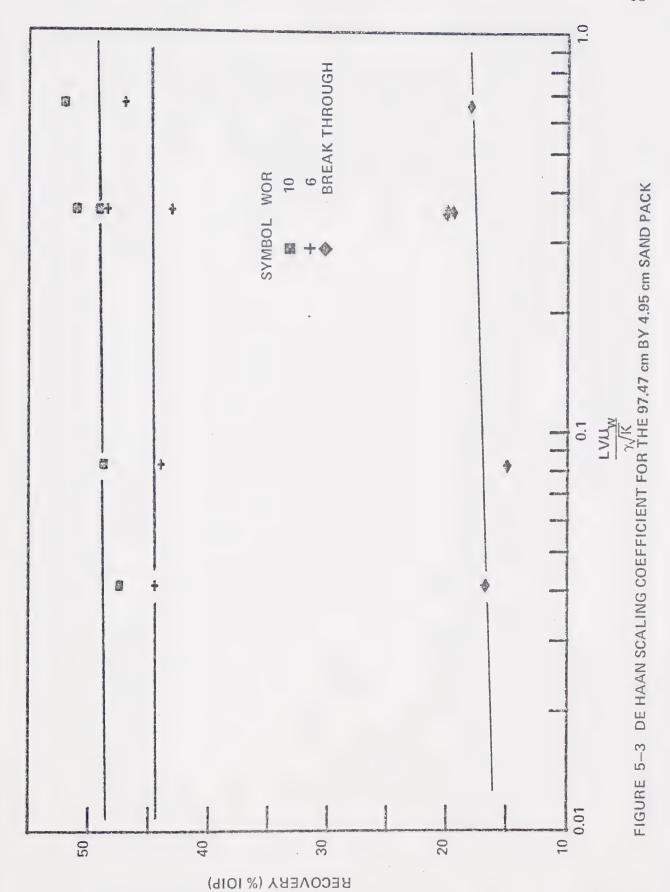


FIGURE 5-2 RAPOPORT AND LEAS SCALING COEFFICIENT FOR THE 97.47 cm BY 4.95 cm SAND PACK







M

A

SYMBOL WOR

6 BT



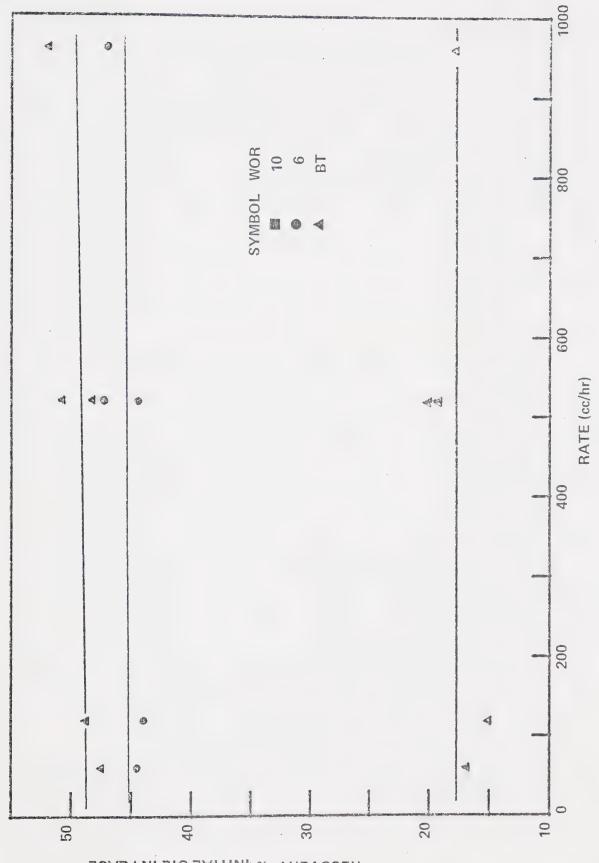


Recovery showed no sensitivity to rate as exhibited by Figure 5-5. This lack of sensitivity of recovery to rate would indicate that there is little or no viscous fingering at injection rates from 60 cc/hr to 960 cc/hr for this system.

As a result of the above investigation a rate of 320 cc/hr was selected for all further displacement tests. This rate was high enough to satisfy Rapoport and Leas' requirement to eliminate capillary end effects (LV $\mu_{\rm W}$  = 20.45 cm<sup>2</sup>cp/min). The de Haan coefficient for the system at 320 cc/hr was 0.22. This is slightly larger than the critical value 0.1 and introduces the possibility of viscous fingering according to de Haan. However, the value of the Chuoke et al. coefficient for this rate was 8.0 which implies no viscous fingering.



FIGURE 5-5



RECOVERY % INITIAL OIL IN PLACE



### EXPERIMENTAL RESULTS

# Sand and Fluid Properties

The Golpher sand used in this study was a clean, coarse grained commercial sand. Its particle size distribution is presented in Figure A-1 and Table A-1. When packed, it formed an unconsolidated core with a porosity of 29 to 32 per cent and a permeability of 37 darcies.

The Sparky sand used was obtained from a lease tank, having been produced with the oil. This introduced the possibility that the Sparky sand had a higher concentration of finer grains and was not equivalent to the natural sand. A sieve analysis of the Sparky sand is presented in Figure A-2 and Table A-2. The particle size distribution shows a much higher percentage of finer grained sand than the natural Sparky sand distribution presented by Scott<sup>41</sup>. Unconsolidated sand packs formed using Sparky sand have porosities of 39 to 43 percent and permeabilities of 21 to 28 darcies.

The properties of the Lloydminster crude used are presented in Table A-3. Viscosity and density as a function of temperature are presented in Figures A-3 and A-4 respectively. The Lloydminster crude oil had



an API gravity of 16.1 degrees and contained 0.18 percent bottom sediments and water.

An artificial brine was used in all displacement tests. It had viscosities of 0.75 centipoise, 0.81 centipoise and 0.99 centipoise at 105°F, 83°F, 76°F respectively. An analysis of the natural brine is presented in Table A-4.

# Interfacial Tension

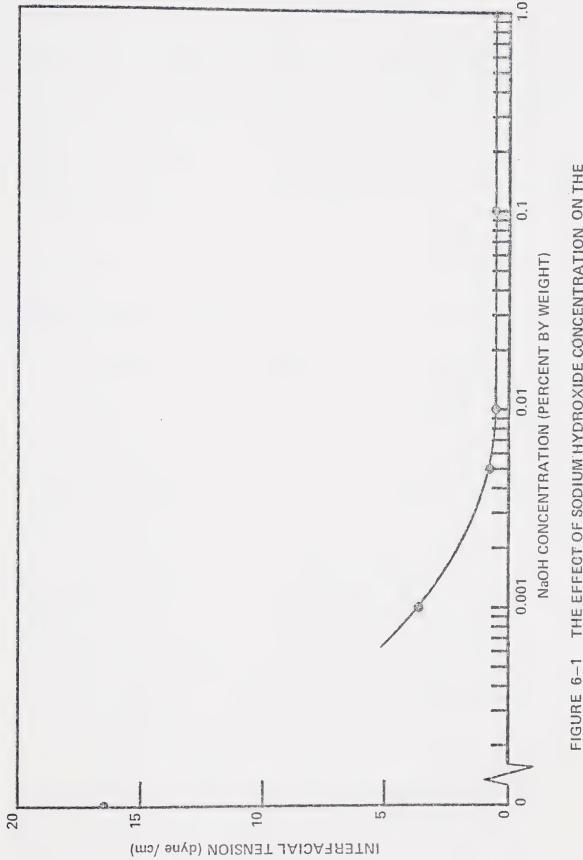
Two sets of interfacial tension data were obtained.

- 1. Lloydminster Crude Sodium Hydroxide in Brine
- 2. Lloydminster Crude Air (surface tension)

The Lloydminster crude - sodium hydroxide in brine interfacial tensions are presented in Table A-5 and Figure 6-1 as a function of sodium hydroxide concentration. The addition of sodium hydroxide to the brine solution rapidly reduced the interfacial tension with the Lloydminster crude. Sodium hydroxide concentrations greater than 0.005 percent reduced the measured interfacial tension below 0.5 dyne/cm (the minimum measurement of the du Noüy tensiometer was 0.5 dyne/cm).

Lloydminster crude - soldium hydroxide in brine





THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE INTERFACIAL TENSION OF LLOYDMINSTER CRUDE OIL



interfacial tension as a function of pH is presented in Figure A-5. This curve was obtained by cross plotting Figure 6-1 with Figure A-6, a plot of sodium hydroxide in brine concentration as a function of pH. At pH values greater than 10.9 the interfacial tension was reduced to a value below 0.5 dyne/cm.

# Wettability Measurements

Bench tests were conducted on fresh Sparky sand and Sparky sand collected from a core that had been subjected to a sodium hydroxide displacement test. Brine, 0.1 percent by weight sodium hydroxide in brine and a 15 percent by volume Lloydminster crude in Varsol solution were used as the imbibing fluids.

Brine did not move into the fresh sand at all; the sodium hydroxide brine solution did not move into the sand any significant amount; however, the crude-Varsol solution readily saturated fresh sand. This would indicate that the fresh Sparky sand as cleaned in this study was preferentially oil-wet.

The brine solution slowly moved into the sodium hydroxide flooded sand; the sodium hydroxide solution moved into the sand at approximately the same rate as the brine; the crude-Varsol solution moved into the



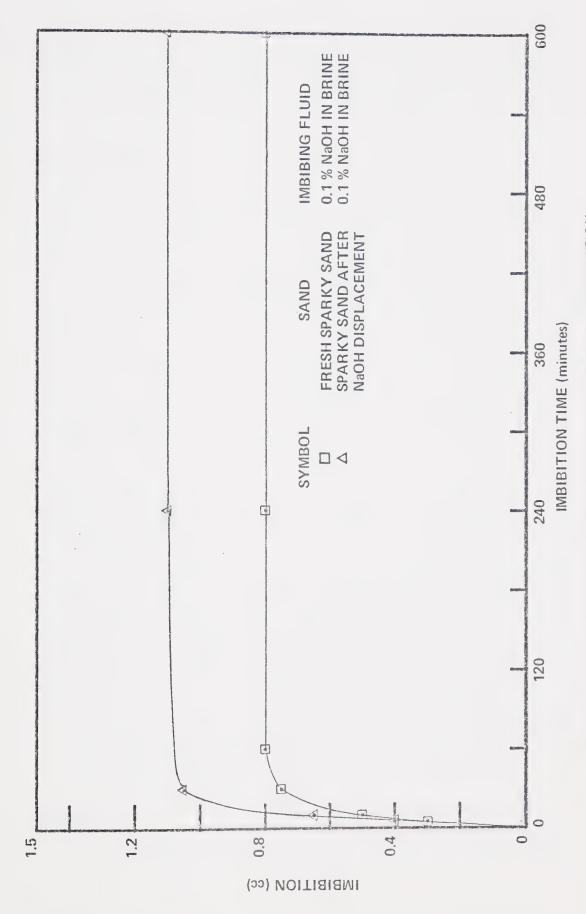
treated sand but less rapidly than it moved into the fresh sand. This would indicate the sand had been made less oil-wet or possibly neutral by the sodium hydroxide displacement test.

Imbibition tests were conducted on both fresh Sparky sand and sand that had been flooded with sodium hydroxide. Brine and 0.1 percent by weight sodium hydroxide in brine solution were used as the imbibing fluid. A 15 percent Lloydminster crude in Varsol solution was used as a saturating solution. An attempt was made to use natural Lloydminster crude as a saturating fluid but no imbibition occurred, probably due to the high viscosity of the crude.

Results of the imbibition tests are presented in Figure 6-2 and Table A-6. Brine would not imbibe into either the fresh Sparky sand or the sodium hydroxide treated sand. The 0.1 percent by weight sodium hydroxide in brine solution imbibed into both fresh and treated Sparky sand. More oil was displaced from the sodium hydroxide treated sand than from the fresh sand. Both brine curves are similar with most of the imbibition occurring in the first thirty minutes of the test.

The results of the bench tests and imbibition tests conducted would indicate that the fresh Sparky sand was preferentially oil-wet and that contact with





THE EFFECT OF SODIUM HYDROXIDE ON THE IMBIBITION RATE OF SPARKY SAND FIGURE 6-2



sodium hydroxide caused a change in wetting, possibly due to a reduction in interfacial tension.

# Core Properties

A summary of the initial conditions of the core used in the displacement tests is presented in Table A-8.

Although it was believed that high values of porosity and permeability might have been due to poor packing
of the cores, inspection of the cores after each displacement test indicated no compaction. A possible explanation is that the grain size was fairly uniform. This
yields a very porous sand pack.

The use of the same core for several displacement tests without cleaning between runs resulted in an increase in the initial water saturation between successive runs. The initial water saturation increased from 7.07 percent in the 1001 run to 29.41 percent for the 1005 and final run on the Golpher sand pack. The same behaviour was observed when a Sparky sand core was flooded twice (runs 2003 and 2004). The first run had an initial water saturation of 7.1 percent, while the second run had an initial water saturation of 20.9 percent.

Relative permeability calculations were made



using the method outlined in Appendix E on the data from displacement tests 6, 8 and 9. Results are presented in Tables E-1 through E-3 and in Figure E-1. The significant shift in the relative permeability curves is observed between the first and the second runs on core 4 (runs 2003 and 2004). This shift was attributed to an increase in the initial water saturation.

All subsequent tests were conducted on fresh sand packs to obtain uniform initial core properties.

This was also made necessary by the fact that sodium hydroxide used in some of the displacement tests might chemically react with the sand changing its properties.

# Displacement Tests

A summary of the displacement tests is presented in Table C-1. The results of the individual tests are presented in Tables D-1 through D-19.

Displacement tests are divided into four series of runs:

- 1. The 1000 series, "scaling factor runs".
- 2. The 2000 series, "base condition runs".
- 3. The 3000 series, "sodium hydroxide base condition runs".
- 4. The 4000 series, "slug injection runs".



The scaling factor runs were used to obtain an injection rate at which capillary end effects and viscous fingering would not affect the displacement test results. As previously mentioned in the section on model scaling, recovery was found to be insensitive to rate for the range tested. An injection rate of 320 cc/hr was selected for all further tests. This rate was high enough not to be affected by capillary end effects and low enough to inhibit viscous fingering.

The 2000 series base condition runs consisted of four displacement tests conducted to obtain a base brine displacement test. All further displacement test data would be compared to this base test to evaluate the effect of sodium hydroxide concentration and adjustment of slug size. Runs 2001, 2002 and 2003 were all conducted at the same conditions and produced similar results. Recovery at water breakthrough ranged from 9.56 to 11.67 percent of the initial oil in place. At 0.5 pore volumes injected, recovery ranged from 20.3 to 26.0 percent of the initial oil in place. Run 2003 was selected as the base brine flood as it represented an average of this series of displacement tests.

Run 2004 was conducted to observe if the same increase of initial water saturation occurred in Sparky sand as that observed in Golpher sand when multiple



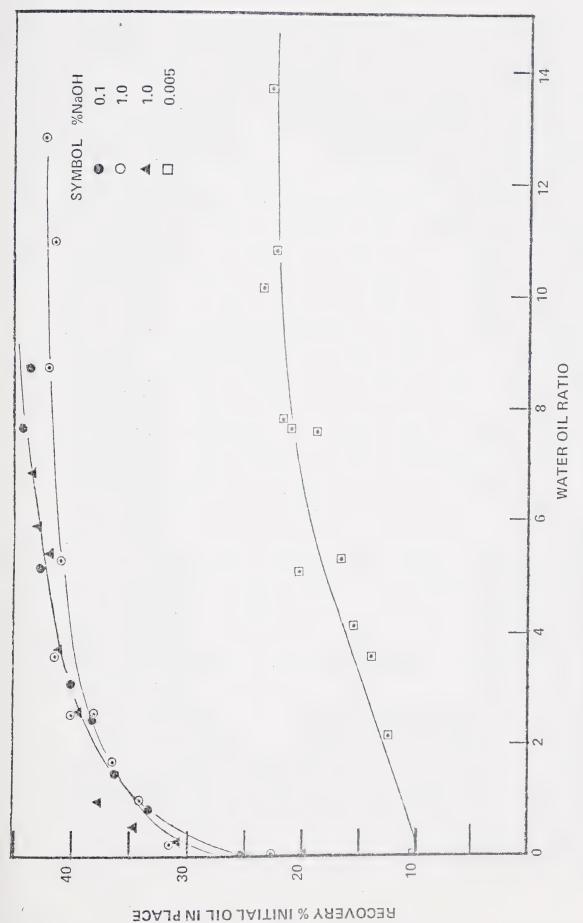
runs were conducted on the same core. Initial water saturation increased from 7.1 to 20.9 percent as previously mentioned in the section on core properties.

Run 2004 was conducted at an injection rate of 480 cc/hr to observe if recovery in Sparky sand was rate sensitive.

No significant differences in results were observed between the tests at 480 cc/hr and tests at 320 cc/hr.

The 3000 series sodium hydroxide base runs were conducted to obtain recovery data on displacement tests employing different concentrations of sodium hydroxide in brine as displacing fluid. Concentrations of 1.0, 0.1, and 0.005 percent by weight sodium hydroxide were The addition of sodium hydroxide to brine resulted in little or no improvement in recoveries for concentrations of 0.005 percent sodium hydroxide or less. concentrations of 0.1 percent sodium hydroxide a 25.45 percent recovery at water breakthrough was observed, a 15 percent increase over that obtained during the base brine flood. At 0.5 pore volume injection recovery was 39.7 percent compared to 23.5 percent for the base brine The use of 1.0 percent sodium hydroxide in brine solution resulted in no significant improvement in recovery compared to the 0.1 percent sodium hydroxide in brine flood. The effect of the use of sodium hydroxide in brine on recovery is illustrated by Figure 6.3. The





RECOVERY AS A FUNCTION OF WATER OIL RATIO FOR DIFFERENT SODIUM HYDROXIDE CONCENTRATIONS FIGURE 6-3



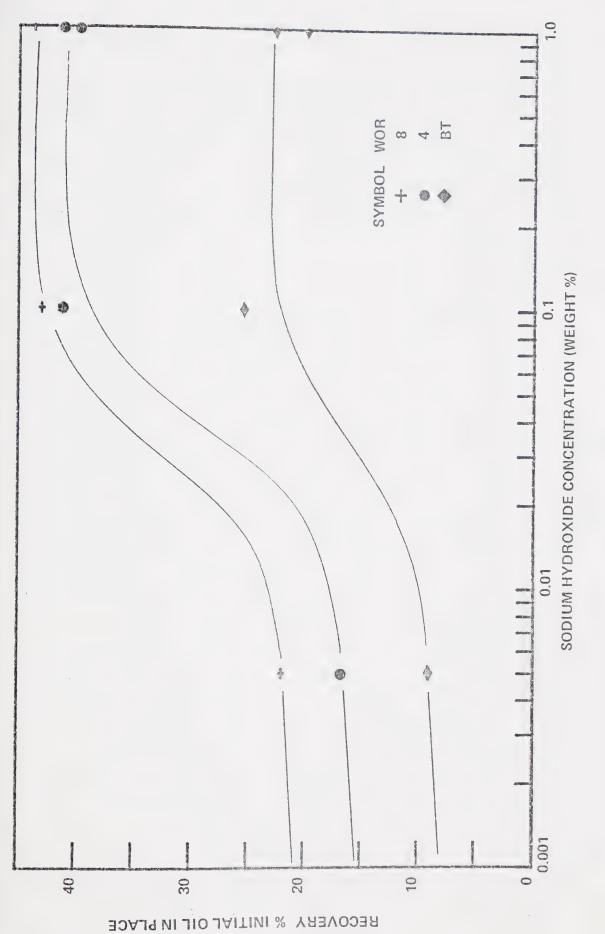
majority of the increase due to sodium hydroxide, occurred prior to water breakthrough. A 9.0 percent breakthrough recovery was achieved with 0.005 percent sodium hydroxide as compared to 19.9 percent or 22.75 percent with 1.0 percent sodium hydroxide and 25.4 percent with 0.1 percent sodium hydroxide. The amount of subordinate recovery after a water-oil-ratio of 5 appears to be the same regardless of sodium hydroxide concentration.

Figure 6-4 illustrates that a minimum sodium hydroxide concentration of approximately 0.1 percent is required to give any significant increases in recovery. Increasing the sodium hydroxide concentration beyond 0.1 percent did not further increase recoveries. Scott 41 obtained similar results flooding with sodium hydroxide in short cores.

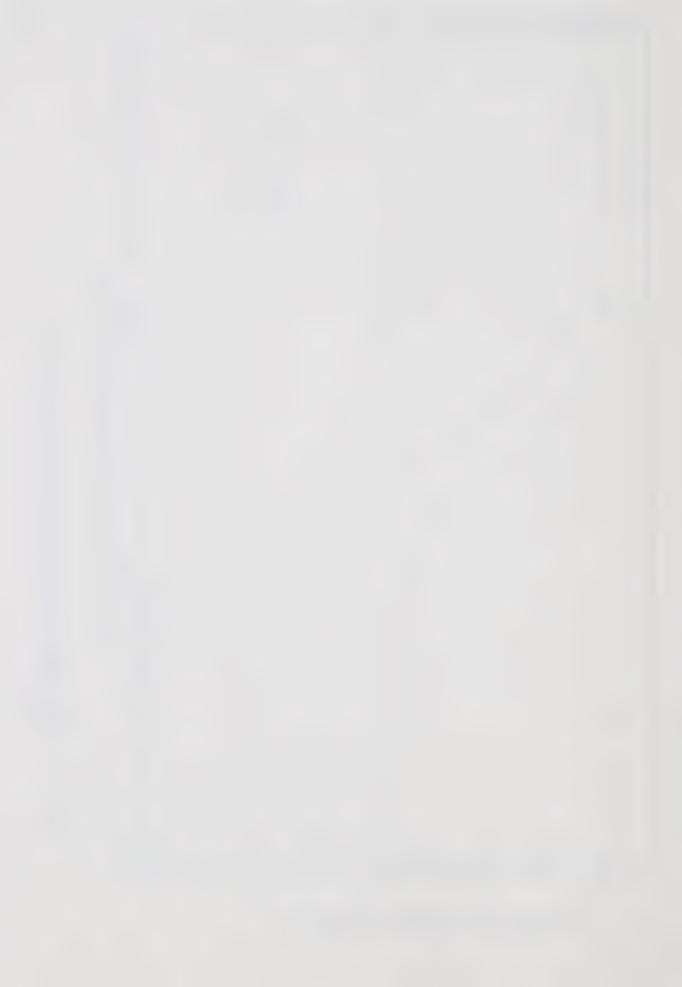
Measurement of effluent pH during the displacement tests showed that the pH was slightly below the injection strength at water breakthrough; shortly after breakthrough the pH rapidly increased to injection strength.

The 4000 series slug injection runs were conducted to investigate the effect on recovery of adding sodium hydroxide to only a portion of the injected fluid. Five displacement tests were run using different slug sizes of 0.1 percent sodium hydroxide brine. The slugs





THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON RECOVERY OF LLOYDMINSTER CRUDE OIL FIGURE 6-4



were pushed through the core by brine injected in the same manner as the sodium hydroxide slugs.

Figures 6-5 and D-1 illustrate the comparative recoveries of the different slug sizes used. Recovery tended to increase with slug size up to 325 cc (0.433 pore volume). The 325 cc (0.433 pore volume), 402 cc (0.536 pore volume), and infinite slug sizes seemed to produce identical recoveries. A cross plot of Figure D-1 presented as Figure 6-6 shows recovery as a function of slug size for three water oil ratios. The optimum slug size, or minimum slug size required to obtain maximum recovery, is approximately 300 cc (0.4 pore volume) for this core system using a sodium hydroxide slug concentration of 0.1 percent. Increasing the slug size above 300 cc (0.4 pore volume), as illustrated in Figure 6-6, did little to improve recovery.

The pH of the effluent was monitored for each different slug size (see Figures D-3 through D-7) and graphed in Figure 6-7. The profile of the pH curves are highly dependent upon slug size. The slugs of 105 cc (0.14 pore volume) and 250 cc (0.33 pore volume) had similar profiles with a rapid drop in pH after water breakthrough, approaching the pH of the brine (7.6). The 325 cc (0.433 pore volume) and 402 cc (0.536 pore volume) slugs had similar profiles, with pH increasing to injection strength (12.0) shortly after breakthrough,



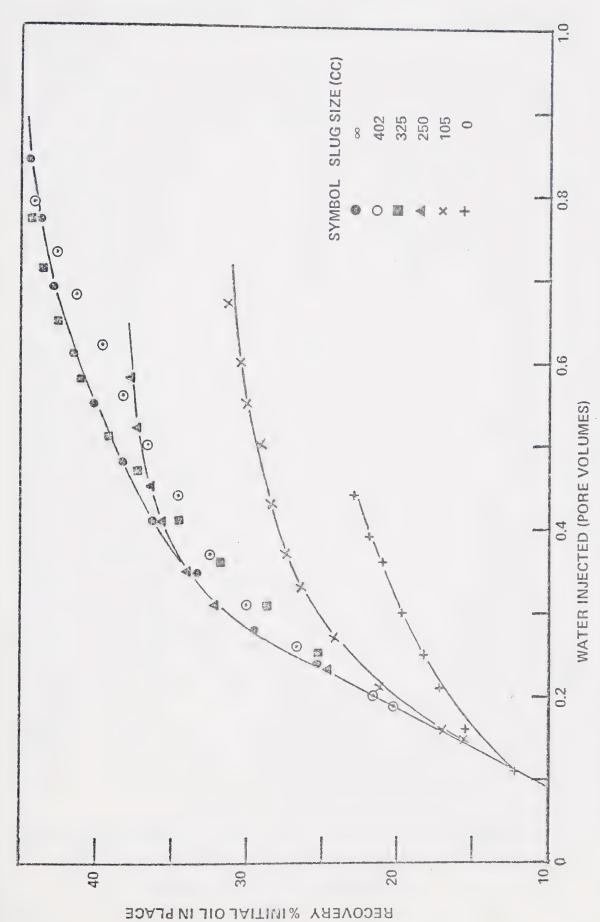
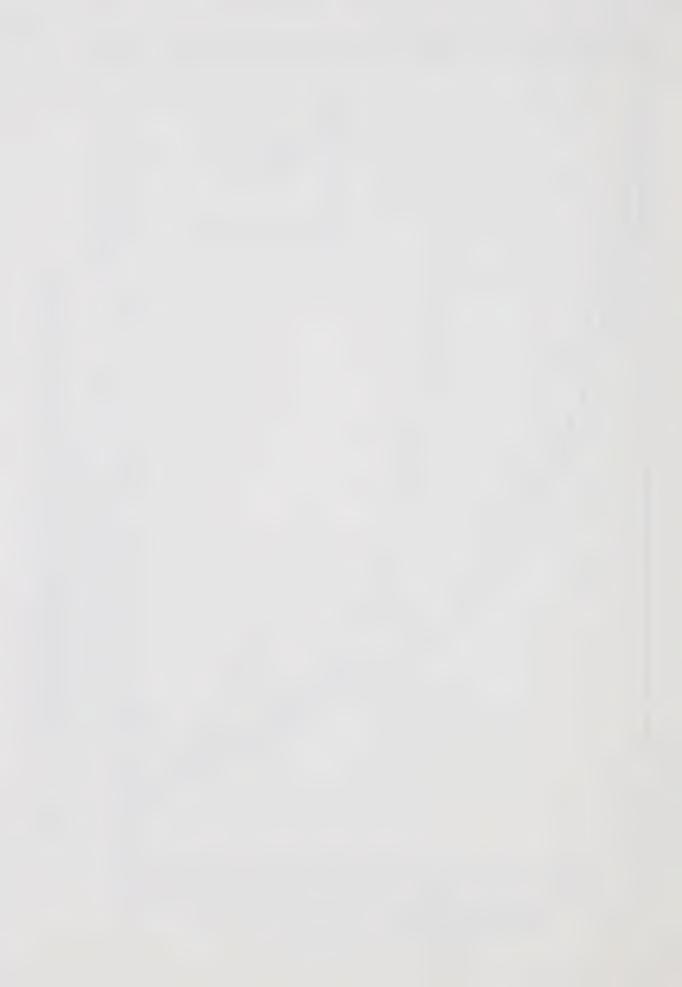
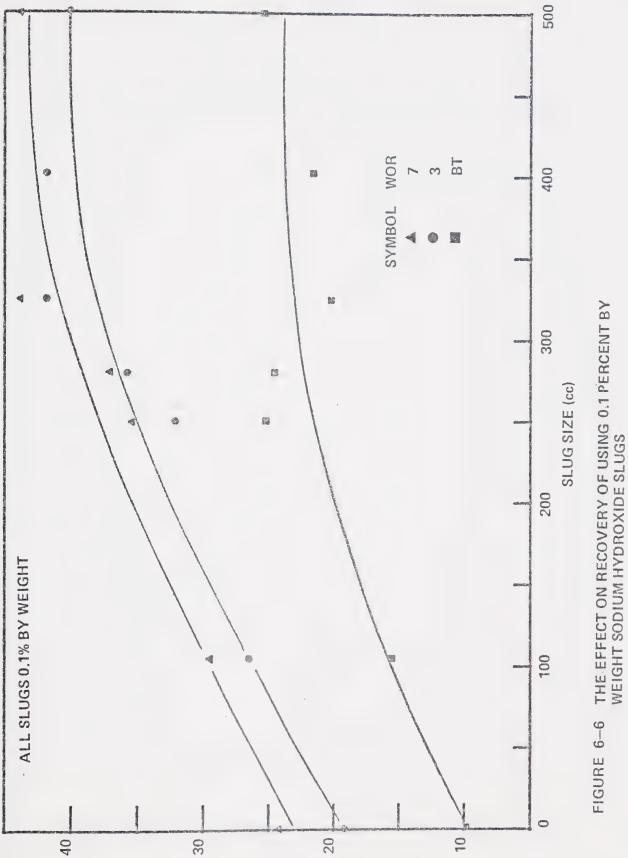


FIGURE 6-5 OIL RECOVERY USING DIFFERENT SLUG SIZES OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE







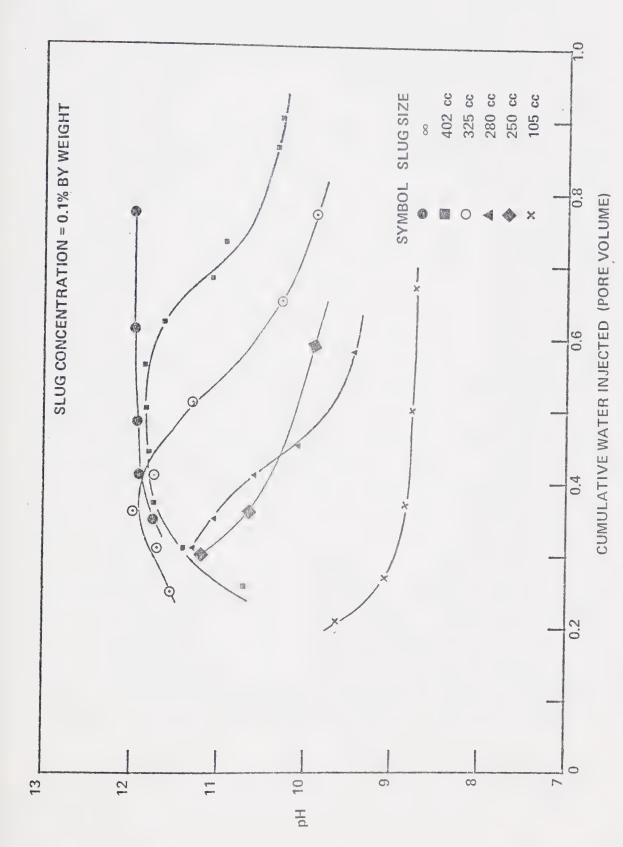


FIGURE 6-7 EFFLUENT pH AS A FUNCTION OF SLUG SIZE



then decreasing to the pH of the brine. The 280 cc (0.373 pore volume) slug seems to be a combination of the two other profiles. For slugs of 105 cc (0.14 pore volume), 250 cc (0.33 pore volume), 280 cc (0.373 pore volume), and 325 cc (0.433 pore volume), increasing the slug size tends to increase the magnitude of the effluent pH. Increasing the slug size from 325 cc (0.433 pore volume) to 402 cc (0.536 pore volume) only resulted in an increase in the amount of full strength, unspent sodium hydroxide in the effluent.

Run 4006 was conducted with a 1.0 percent sodium hydroxide 105 cc (0.14 pore volume) slug to observe the effect on oil recovery of changing slug concentration. The use of 1.0 percent sodium hydroxide resulted in significantly higher recoveries as illustrated in Figures 6-8 and D-2. The recovery at water breakthrough of 17.5 percent was similar to the 0.1 percent slug recovery at breakthrough of 15.55 percent, recovery at 0.5 pore volume injected was 36.0 percent compared to 29.16 percent for the 0.1 percent sodium hydroxide slug. By 0.8 pore volume injected the 105 cc (0.14 pore volume) slug of 1.0 percent sodium hydroxide had a higher cumulative recovery than all the slug sizes less than 325 cc.



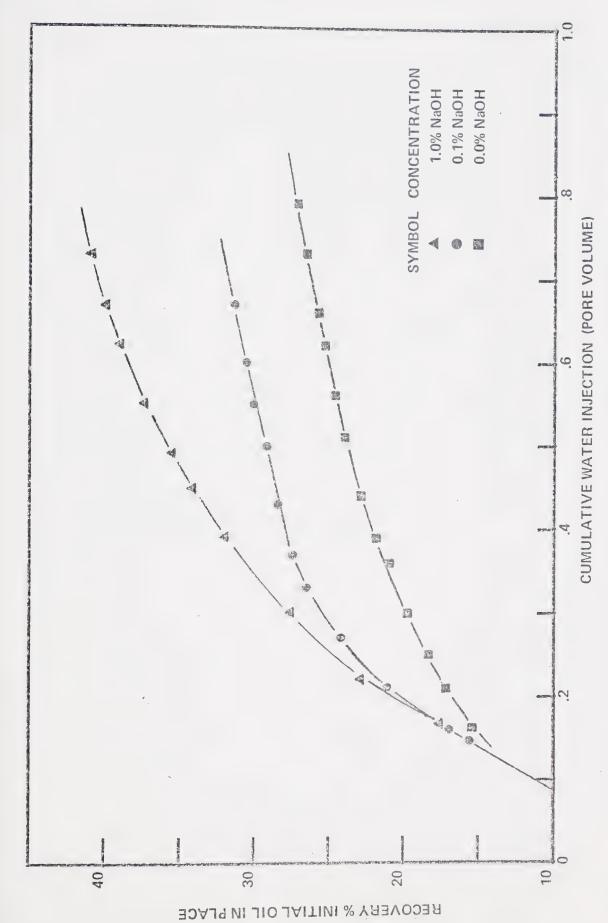


FIGURE 6-8 COMPARISON OF RECOVERY FOR DIFFERENT CONCENTRATIONS IN 105 cc SLUGS



The pH profile of the effluent during the 105 cc (0.14 pore volume) slug runs is presented in Figure 6-9. Both the 1.0 percent sodium hydroxide slug and the 0.1 percent sodium hydroxide slug have similar profiles except for the curve shift due to differences in slug concentration. The pH decline of the 1.0 percent curve was less rapid right after breakthrough but continues longer than the 0.1 percent curve. The effect of different concentrations of sodium hydroxide in the slug is illustrated in Figure 6-10. Although the number of data points is limited, it appears that recovery at breakthrough is not sensitive to slug concentration above 0.1 percent sodium hydroxide. Recoveries at water-oil ratios of 3.0 and 7.0 increase gradually as slug concentration is increased.



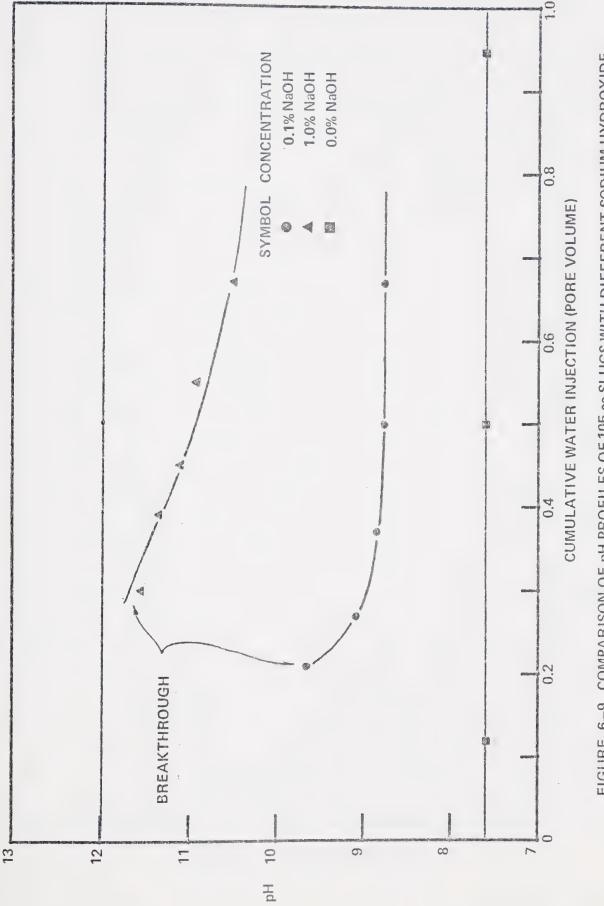
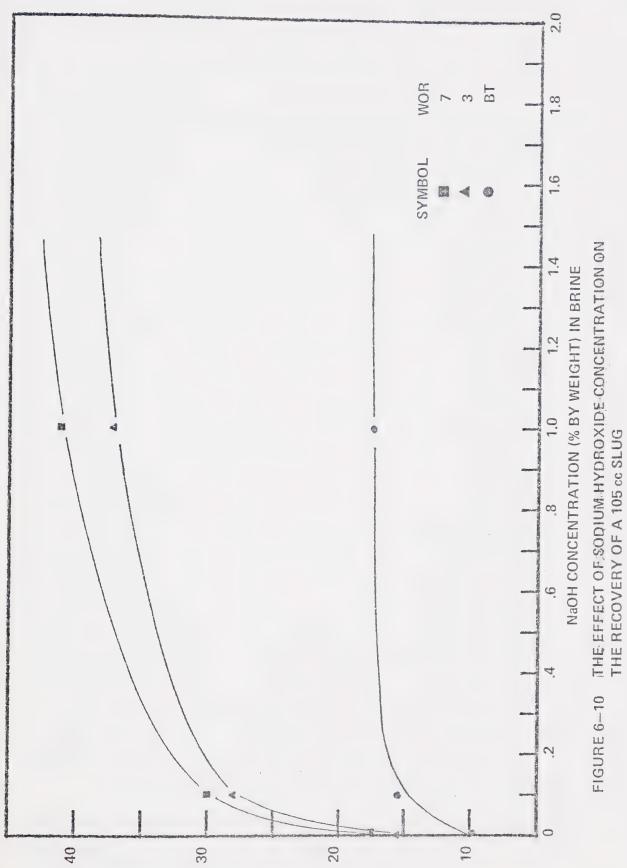


FIGURE 6-9 COMPARISON OF pH PROFILES OF 105 cc SLUGS WITH DIFFERENT SODIUM HYDROXIDE CONCENTRATION





RECOVERY % INITIAL OIL IN PLACE



## DISCUSSION

In previous studies employing sodium hydroxide as an additive to increase water flood recovery several reasons have been given for increased recovery. Some authors 36,3 have stated that increased recovery is due to a change of wetting caused by chemical reaction at the sand surface. This would result in the removal from the sand surface of oil that previously would not be recovered. Other authors 4,45,46 have suggested increased recovery was due to the reduction of the oilwater interfacial tension, making it easier to push the oil droplets through the constrictions in the pores of the porous medium.

Scott<sup>41</sup>, in his study, suggested that an oil-water emulsion was formed in the core by the sodium hydroxide solution, plugging the path of least resistance. This would force the displacing fluid into more resistant paths that would in turn be plugged by the emulsion until all paths are plugged. The emulsion would then be pushed through the core, displacing oil ahead of it (improved mobility ratio).

Reisberg et al. <sup>39</sup> found that sodium hydroxide reacted with the components of Ventura crude to change the wetting characteristics of the sand.



Both a change in wetting and a reduction of interfacial tension were observed in this study. The Sparky sand used was initially oil-wet according to the results of the imbibition and bench tests. Wettability tests conducted on the sand after it had been contacted by the sodium hydroxide indicated that it had been made less oil-wet. The shift in the relative permeability (Figure E-2) obtained when sodium hydroxide was used in the displacing phase seemed to confirm a wetting change.

Very low concentrations of sodium hydroxide in brine reduced Lloydminster crude - sodium hydroxide in brine solution interfacial tension to very low values, as illustrated in Table A-5. Concentrations greater than 0.005 percent sodium hydroxide in brine resulted in interfacial tension values less than the minimum measureable value with the du Noüy tensiometer of 0.5 dyne/cm.

It is possible that increased recoveries are due to both a wetting change and a reduction of the interfacial tensions. It should be noted that wettability and interfacial tension are interrelated and an adjustment to one would affect the other.

Whatever the displacement mechanism may be, it is evident that there is a minimum sodium hydroxide concentration required in order to increase recovery.



If the concentration is less than the minimum required, the displacement mechanism is not significantly activated and only minimal increases in recovery are realized. If only a portion of the core is contacted by sodium hydroxide solution with the minimum required concentration then increased recoveries are obtained from only that portion of the core.

Tests conducted using sodium hydroxide added to the entire injected fluid indicated that an approximate minimum injection concentration of 0.1 percent by weight sodium hydroxide is required for the system used in the study. An exact value of the minimum required concentration is impossible to obtain due to concentration changes after the solution has entered the core. The sodium hydroxide injection concentration must be high enough to compensate for dilution, reaction losses and absorption to allow the whole core to be contacted by sodium hydroxide solution with a concentration greater than the minimum required.

If sodium hydroxide is added to the entire injected fluid, as in the 3000 series of runs, maximum recoveries will result as long as the injection concentration is higher than the minimum required concentration. All the reservoir will be contacted by the injected fluid with the minimum required concentration.



Although the produced effluent at breakthrough had a reduced pH due to dilution, adsorption, and possibly chemical reaction, the effluent pH increased to injection strength when more of the displaced phase was produced. Since this indicates that injected fluid is passing through the core without loss of sodium hydroxide to reaction, dilution and adsorption, it can be assumed that no significant amount of unflooded core is being contacted.

The addition of sodium hydroxide to all of the injected fluid is unnecessary. A slug of sodium hydroxide solution displaced through the core by brine, if properly designed, would obtain the same increased recovery.

The slug must contain enough sodium hydroxide to provide for all losses in the core from injection to production, while maintaining a sodium hydroxide concentration higher than the minimum required concentration. There are two possible methods of achieving this. The first is to inject a large low-concentration slug; the second is to inject a small high-concentration slug (small, high concentration slugs tend to be more sensitive to fingering and bypassing). In the study, it was assumed that the recovery achieved when using an infinite slug (sodium hydroxide added to all the injected fluid)



of 0.1 percent sodium hydroxide brine solution was the maximum recovery possible with sodium hydroxide solutions. This recovery was used as a comparison for subsequent tests using different slug sizes.

Slugs of 325 cc (0.433 pore volume) and 402 cc (0.536 pore volume) of 0.1 percent sodium hydroxide, pushed through the core by brine, produced recoveries equal to that of the infinite slug. The 280 cc (0.373 pore volume) and smaller slugs produced only a portion of infinite slug recovery. It can be concluded that for this system the optimum 0.1 percent sodium hydroxide slug size is approximately 300 cc (0.40 pore volume) as indicated by Figure 6-6.

Inspection of the effluent pH profile (Figure 6-7) of the different slug sizes indicates that the best recoveries were obtained when the effluent pH approached the injection pH of 11.98, at or after breakthrough.

For the 325 cc (0.433 pore volume), 402 cc (0.536 pore volume) and infinite slug sizes, effluent pH values of 11.8 or greater were measured. The smaller, less successful, slug sizes had effluent pH values much smaller than the injected pH. This would indicate that smaller slug sizes were being used up, or dissipated, prior to breakthrough. The dissipation of the slug could be due to the expected dilution, adsorption and chemical



reaction using up the sodium hydroxide at the leading edge of the slug. It could also be caused by fingering of the pushing brine at the trailing edge of the slug.

The pH profile of the 325 cc (0.433 pore volume) and 402 cc (0.536 pore volume) slugs exhibit low pH values at breakthrough which would indicate that the chemical in the leading edge of the slug is being used up.

The slow drop in pH at the trailing edge of the slug might be interpreted as being due to mixing of the slug and the pushing brine which is a miscible type of displacement (i.e. water displacing water). The fluctuation of water-oil ratio (Figure D-1) could also be attributed to mixing at the trailing edge of the slug.

It is possible that if mixing by the pushing brine was negated, much smaller, more economical slugs could achieve maximum recoveries. Mixing at the trailing edge of the slug could be drastically reduced by separating the sodium hydroxide slug and the pushing brine with a mobility buffer of polymers similar to that used in micellar-slug flooding.

Results of the use of a 105 cc (0.14 pore volume) slug of 1.0 percent sodium hydroxide suggested that increasing the slug concentration greatly improved the recovery of small slugs. The pH profile (Figure D-7)



indicates that this increased sodium hydroxide concentration makes it possible for the slug to withstand more mixing than the 0.1 percent sodium hydroxide before dropping below the minimum required concentration. The higher concentration would initially result in sharp concentration change in the core which, according to Moore et al. 4 would achieve higher recoveries.

A calculation was made for an idealized system (Appendix F) based on the results of the study to estimate the increased recovery and the amount of sodium hydroxide required for an oilfield scale enhanced recovery project. Linear displacement and 100 percent volumetric sweep were assumed. It was found that, by injecting a 0.4 pore volume slug of 0.1 percent sodium hydroxide in water, 384,300 barrels could be recovered from 40 acres of 10 foot thick Lloydminster-Sparky reservoir at a water-oil-ratio of 10. This would require 135,235 pounds of sodium hydroxide in a 450,000 barrel slug.



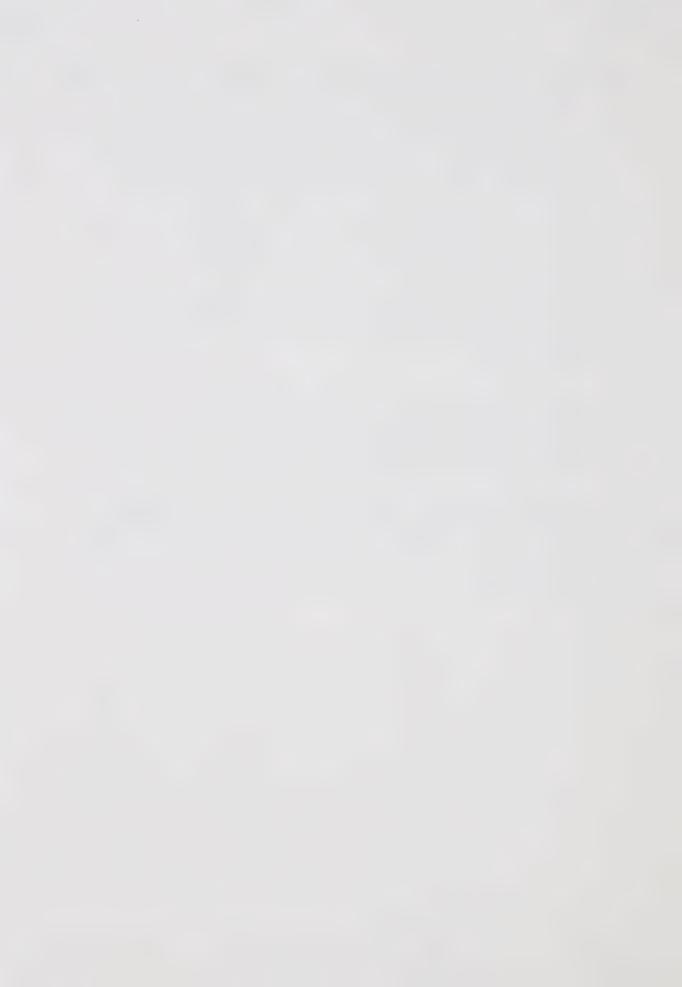
### CONCLUSIONS

The following conclusions are based on the results of this experimental investigation of the effects of sodium hydroxide slug size and concentration on the recovery of viscous crude oil.

- 1. Recoveries of 40-45 percent of the initial oil-in-place can be achieved at a water-oil ratio of 10 when sodium hydroxide in sufficient concentrations is injected into a clean, sorted, Sparky sand core saturated with Lloydminster crude. A previous investigation by Scott 41 obtained similar results.
- 2. Concentrations of 0.005 percent sodium hydroxide in brine will lower Lloydminster crude oil interfacial tension to less than 0.5 dyne/cm. These results are similar to those obtained by Cooper<sup>11</sup> and Scott<sup>41</sup> in previous investigations.
- 3. To obtain significant increases in recovery from a Lloydminster-Sparky sand type system when flooding with sodium hydroxide in brine, concentrations of 0.1 percent by weight sodium hydroxide are required confirming results previously presented by Scott 41.



- 4. A 0.4 pore volume slug of 0.1 percent by weight sodium hydroxide in brine followed through the core by brine achieves a recovery equivalent to that of an infinite slug of 0.1 percent sodium hydroxide.
- 5. Extensive dilution occurs at the trailing edge of the sodium hydroxide slug due to mixing.
- 6. Increasing the sodium hydroxide concentrations of the smaller slug sizes will result in increased recoveries.
- 7. Tests conducted on the Sparky sand used in this study indicate that it was preferentially oil-wet confirming similar results presented by Scott 40 and Scott 41.
- 8. Sodium hydroxide, in contact with an oil-wet sand system, will cause the sand to become less oil-wet, or neutral.



### RECOMMENDATIONS .

From the data presented in this thesis the following recommendations can be made:

- 1. A further reduction of the required slug size can be achieved if fingering at the trailing edge of the sodium hydroxide slug was inhibited. Use of a polymer mobility buffer to separate the sodium hydroxide and the brine should be investigated.
- 2. Further study should be directed at the possibility of increasing recovery by the use of small, high concentration slugs of sodium hydroxide.
- 3. As viscous fingering is a function of the velocity at which one fluid displaces another, it is possible that lower injection rates would reduce the amount of mixing at the trailing edge of the slug. The effects of various injection rates on mixing of the brine into the sodium hydroxide slugs should also be investigated. It should be noted that actual reservoir velocities are low and decrease with distance from the injection well.



- 4. More knowledge of the actual microscopic effects of injecting sodium hydroxide into a porous medium saturated with viscous crude oil would be invaluable. To properly design a sodium hydroxide recovery process the displacement mechanism and its effects on the fluid properties must be known.
- 5. In order for sodium hydroxide to be used as a reservoir recovery process, further investigation of the interaction between the sodium hydroxide and natural field water should be condicted. Previous investigators have indicated that mixing of sodium hydroxide with field water has resulted in formation of a precipitate.
- 6. The use of sodium hydroxide causes the production to be in the form of an emulsion and further studies should be conducted on emulsions and methods of breaking emulsions. In this study, sodium hydroxide injection was treated as a primary recovery process.
- 7. Further tests should be conducted on flooded-out cores to observe if sodium hydroxide injection is applicable as a secondary recovery process.

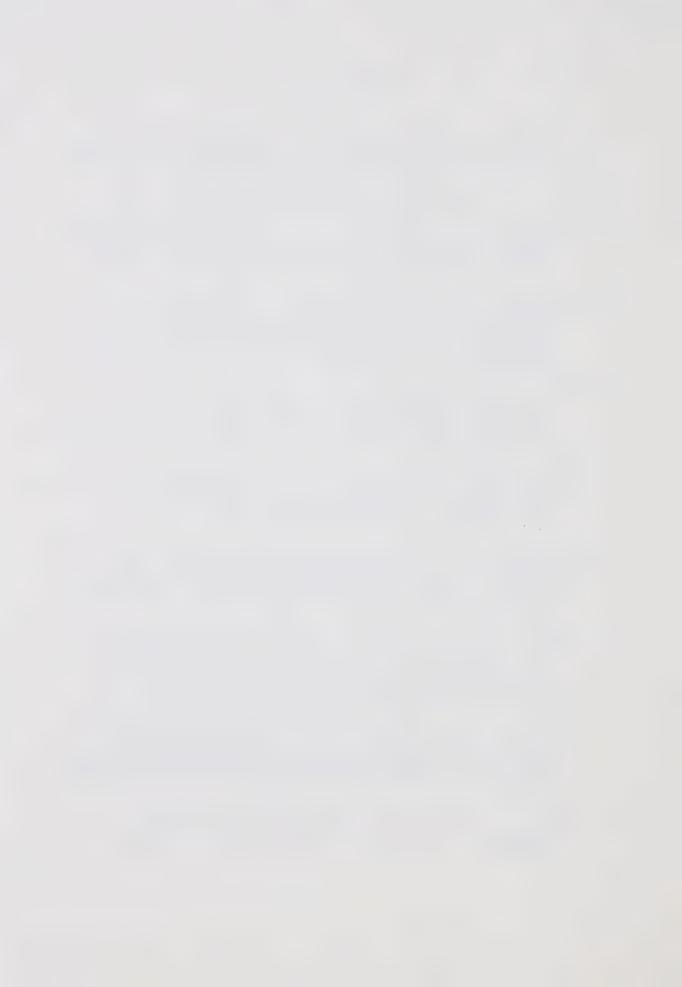


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# APPENDIX A

PHYSICAL PROPERTIES OF THE ROCKS AND FLUIDS

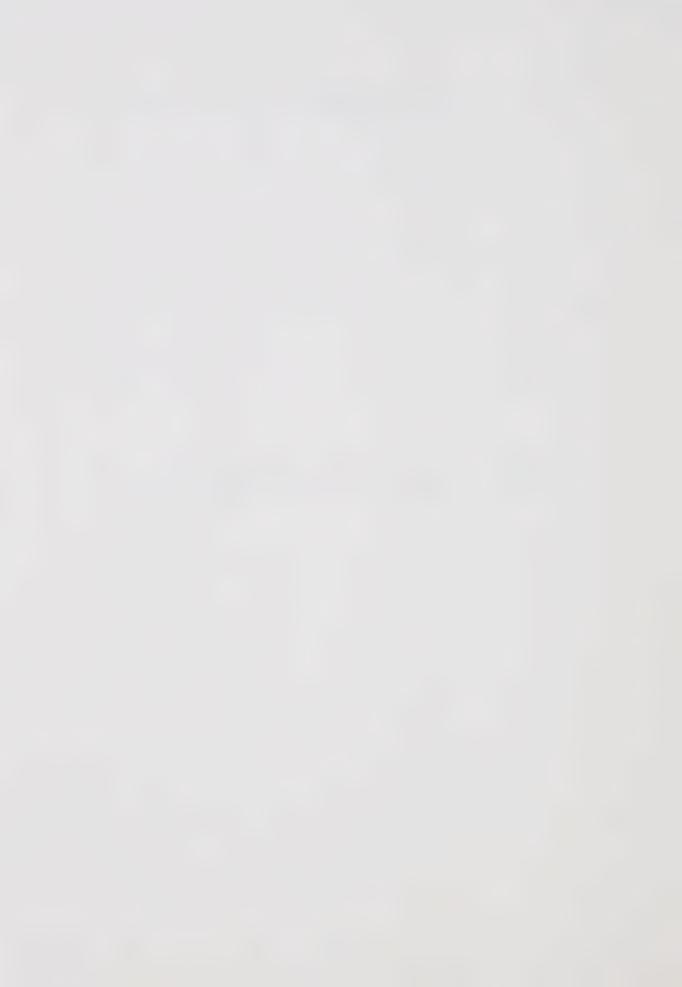


TABLE A-1

Golpher Sand				
Mesh Size	Aperature Diameter (inches)	Weight Retained (gms)	Weight Flow Through (gms)	Cumulative Mass Fraction Through Screen
14	1.41		869.5	1.0
20	0.841	8.5	861.0	0.9902
28	0.595	526.2	334.8	0.385
35	0.50	295.7	39.1	0.0454
48	0.297	34.6	4.5	0.0052
100	0.149	4.5		
		869.5		

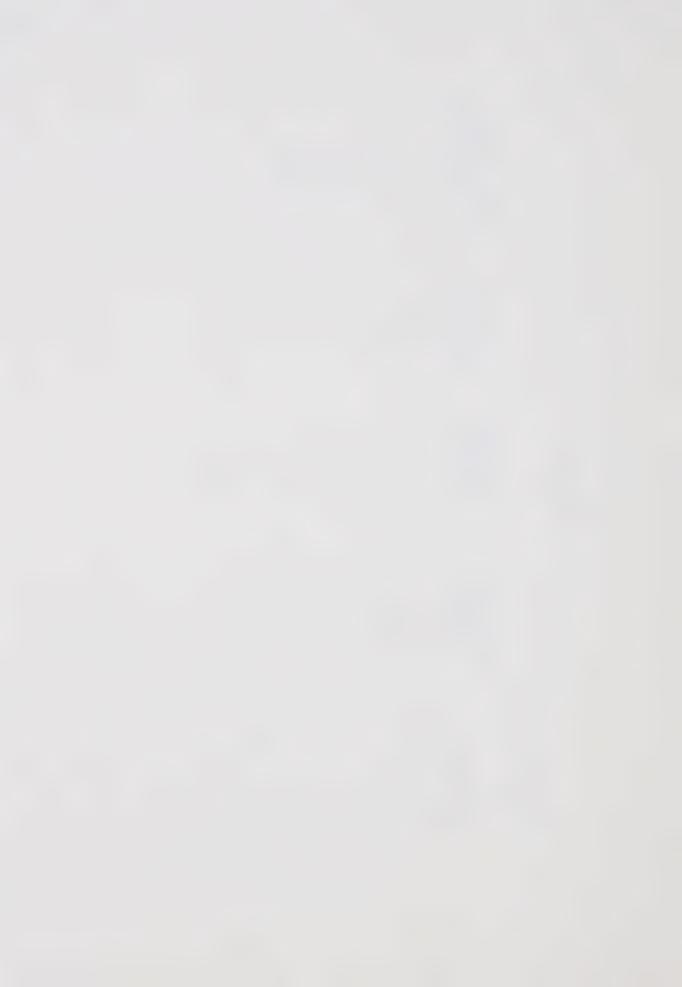


TABLE A-2

Sparky Sand				
Mesh Size	Aperature Diameter (inches)	Weight Retained (gms)	Weight Flow Through (gms)	Cumulative Mass Fraction Through Screen
35	0.5		326.8	1.00
48	0.297		326.8	1.00
65	0.213	153.8	173.0	0.5294
100	0.149	110.3	62.7	0.1919
150	0.100	48.4	14.3	0.0439
200	0.074	14.3		
		326.8		



TABLE A-3

Viscosity of Lloydminster Crude

Temperature °F	Viscosity, Cp
70.16	1780.95
90.00	932.82
122.00	239.86
147.20	96.46

# Density of Lloydminster Crude

Temperature, °F	Density, gm/cc
70.16	0.9560
90.00	0.9495
122.00	0.9356
147.20	0.9115



### TABLE A-4

# Chemical Water Analysis

Lloydminster	(Sparky	Pool)

Conductivity	87,000	ppm
Total Solids	73,936	ppm
Hardness	9,850	ppm
Chlorides	44,400	ppm ·
Alkalinity	40	ppm
		Bicarbonate of Calcium and Magnesium
Iron	18.25	ppm
IronCalcium		**
	2,640.0	) ppm
Calcium	2,640.0 1,150.0	) ppm
Calcium	2,640.0 1,150.0 23,000	) ppm

ppm

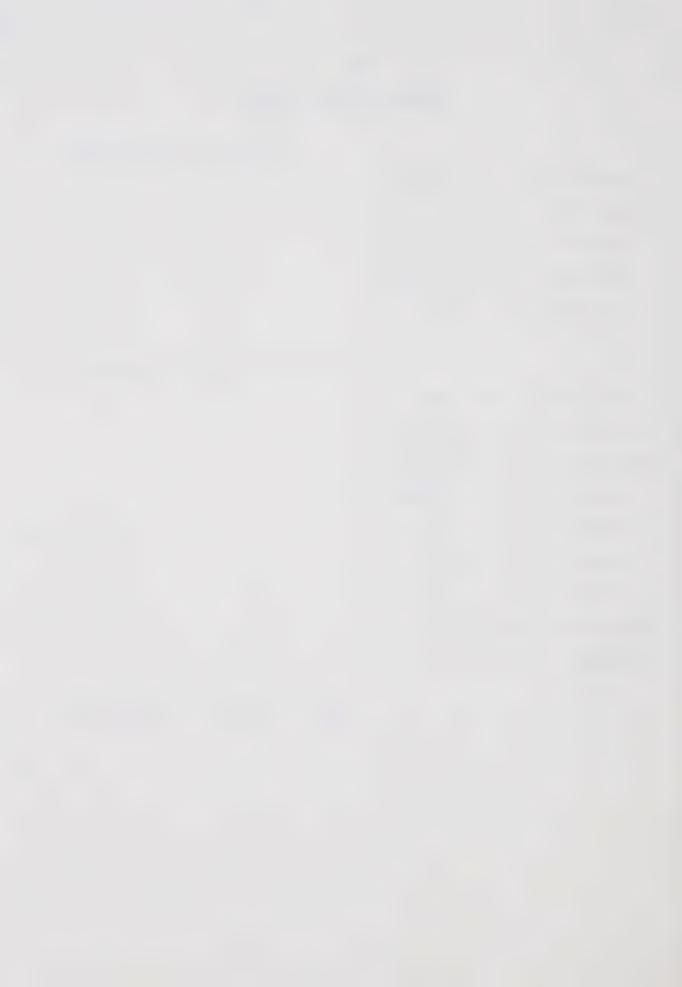
ppm

ppm

Manganese----0.4

Sulfates-----4.0

Alberta Department of Agriculture



# TABLE A-5

# Interfacial Tension

 $T = 76^{\circ}F$ 

Concentration Sodium Hydroxide (percent by weight)	Interfacial Tension (dyne/cm)
1.0	0.5
0.5	0.5
0.1	0.5
0.05	0.5
0.01	0.5
0.005	0.6
0.001	3.6
0.000 (Brine)	16.5

## Surface Tension

T = 76°F

Brine	76.6	dyne/cm
Lloydminster Crude Oil	28.1	dyne/cm



TABLE A-6

## Wettability Measurements

## Bench Test

Sand	Fluid	Rate	of Movement Sand	Into
Fresh Sparky	Brine		Nil	
	Varsol-Crude		Spontaneous	
	Sodium Hydroxide- Brine		Nil	
Sodium Hydroxide Contacted Sparky	Brine		Slow	
Sand	Varsol-Crude		Rapid	
	Sodium Hydroxide- Brine		Rapid	

### Imbibition Test 1

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Fresh Sparky Sand.

Imbibing Fluid = Brine.

Time, Min.	Total Imbibition, cc
0	0.0
5	0.0
10	0.0
30	0.0
60	0.0
240	0.0
600	0.0



### Imbibition Test 2

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Fresh Sparky Sand.

Imbibing Fluid = 0.1 percent by Weight Sodium Hydroxide in Brine.

Time Min.	Total Imbibition cc	
0	0.0	
5	0.3	
10	0.5	
30	0.75	
60	0.8	
240	0.8	
600	0.8	

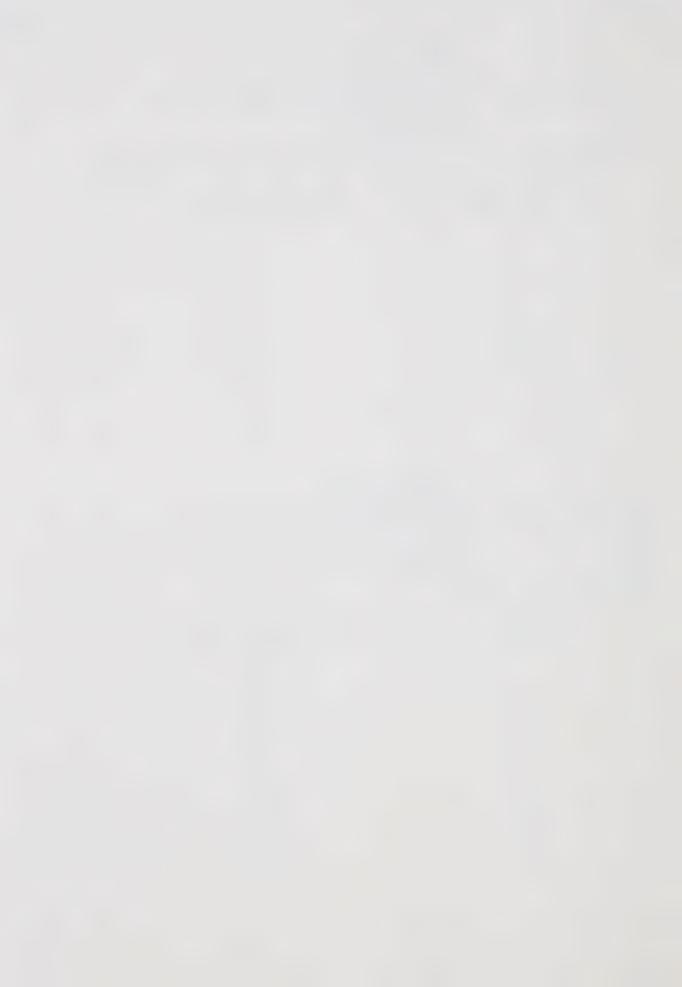
## Imbibition Test 3

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Sparky Sand Treated with Sodium Hydroxide

Imbibing Brine = Brine.

Time Min.	Total Imbibition cc
0	0.0
5	0.0
10	0.0
30	0.0
60	0.0
240	0.0
600	0.0



## Imbibition Test 4

Saturating Fluid = 15 percent Lloydminster Crude in Varsol.

Sand = Sparky Sand Treated with Sodium Hydroxide

Imbibing Fluid = 0.1 percent by Weight Sodium Hydroxide in Brine.

Time, Min.	Total Imbibition, cc
. 0	0.0
5	0.4
10	0.65
30	1.05
60	1.05
240	1.1
600	1.1



TABLE A-7

# pH as a Function of Sodium Hydroxide Concentration

Sodium Hydroxide Concentration, weight percent	рН
1.0	12.88
0.5	12.45
0.1	11.98
0.05	11.80
0.1	11.21
0.005	10.90

Temperature 76°F

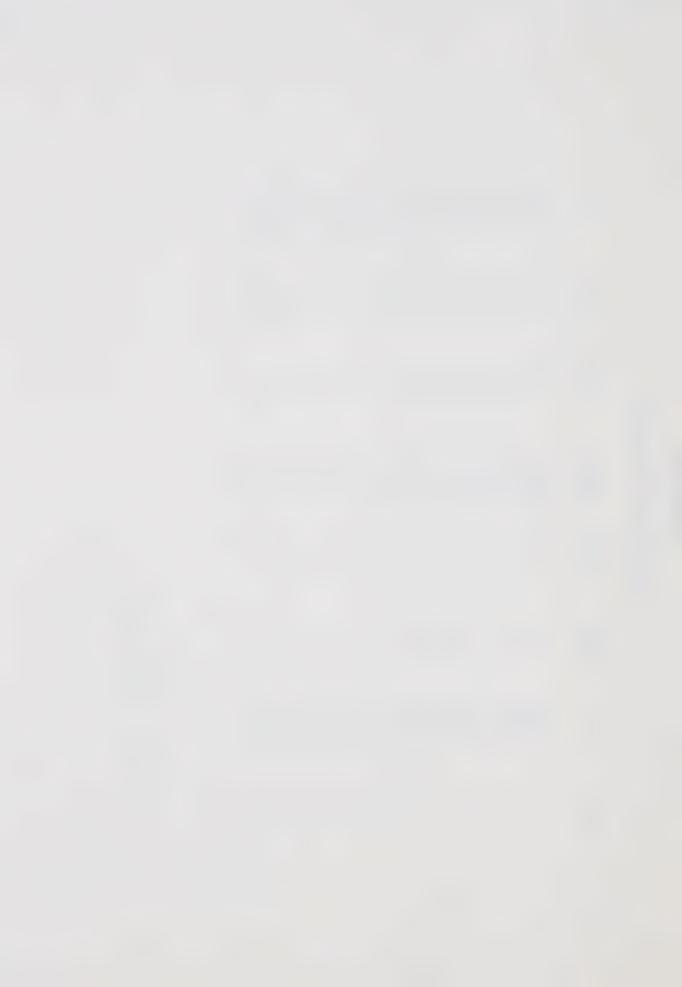


Initial Core Properties

TABLE A-8

8	32.45 32.45 32.45	32.45	39.18	44.43	41.63	43.90	39.71	43.47	40.92	47.88
K	37.73 37.73 37.73	37.73 37.73	24.50	28.37	27.00	27.47	26.41	22.46	21.82	77.00
Swi % P.V.	7.0 15.5 15.9	17.7 29.4 8.6	6.4	20.9	7.1	7.8	6.4	6.1	, 00 ,	5.5
TEMP.	102.0 103.0 103.0	102.0 106.0 85.0	86.9	0.7.0	85.0	85.0	88.0	87.0	86.0	000
CORE		H H N	164	4	9	7 8	9	11	133	T+
SAND		<del>니</del> .	1212	2 0	7 7	7 7	7 7	2 5	170	7
RUN	, 1001 , 1002 1003	1004 1005 2001	2002	2004	3002	3003 3004	4001 4002	4003	4005	4000
TEST	3 2 1	459	7 8	6		12	14	16	18	17

\* Sand Type 1 = Golpher Sand Sand Type 2 = Sparky Sand



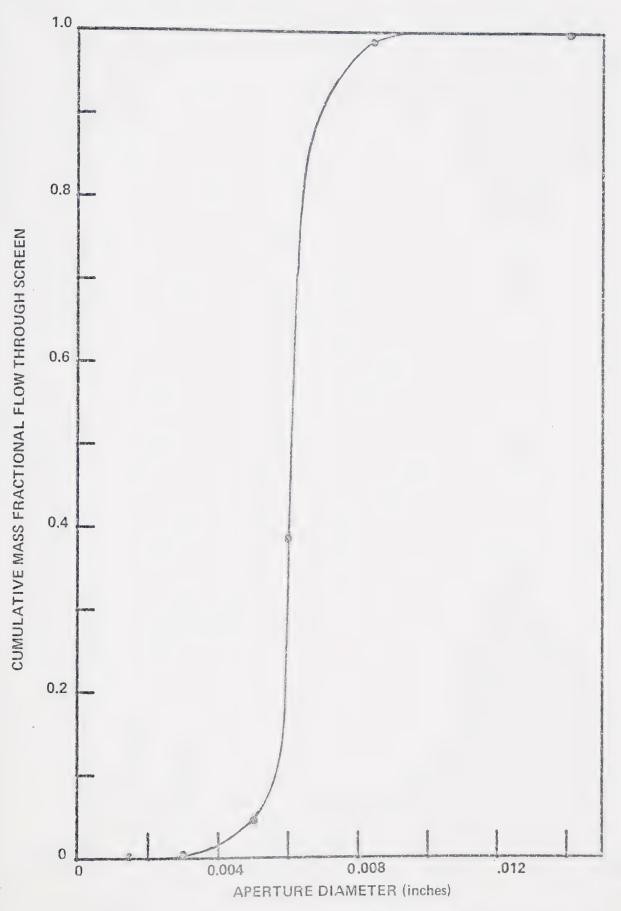


FIGURE A-1 PARTICLE SIZE DISTRIBUTION OF GOLPHER SANDS



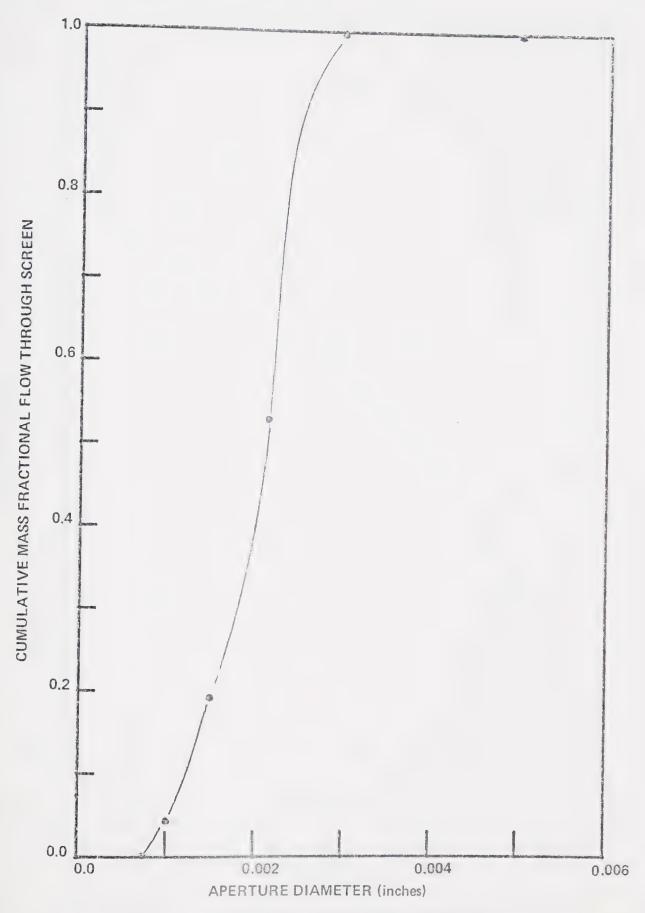
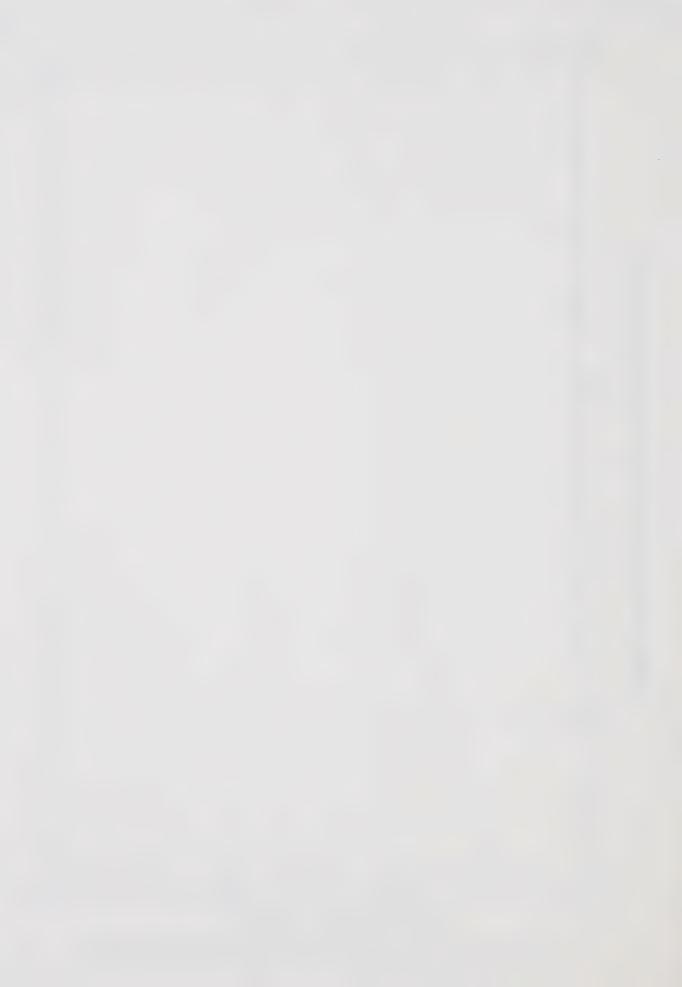


FIGURE A-2 PARTICLE SIZE DISTRIBUTION OF SPARKY SAND



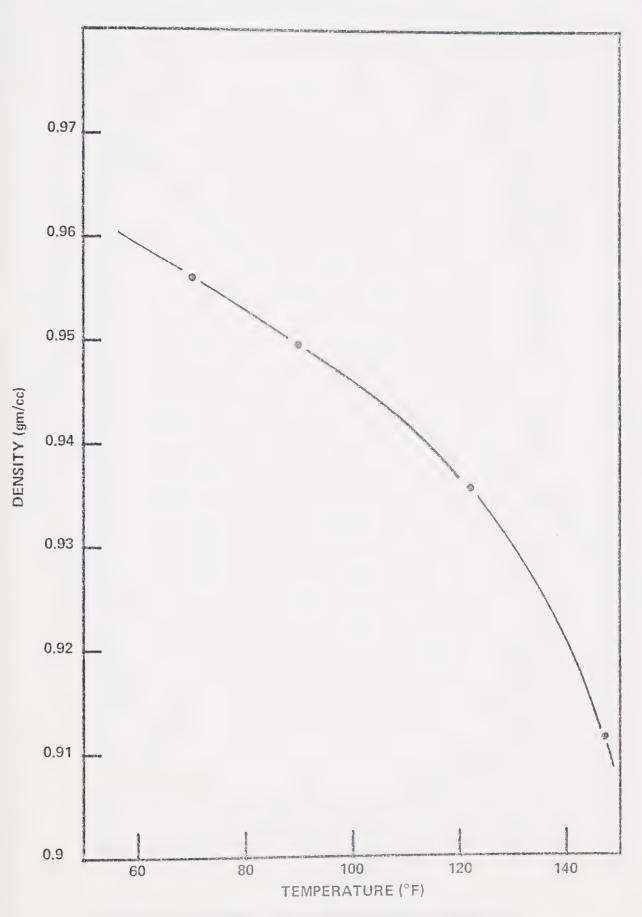


FIGURE A-3 DENSITY OF LLOYDMINSTER CRUDE AS A FUNCTION OF TEMPERATURE



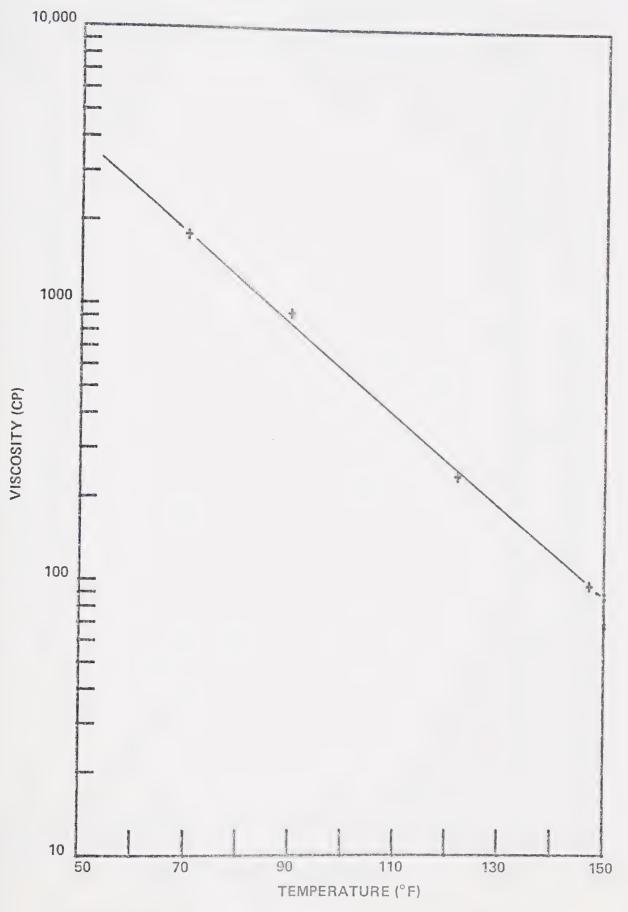


FIGURE A-4 VISCOSITY OF LLOYDMINSTER CRUDE AS A FUNCTION OF TEMPERATURE



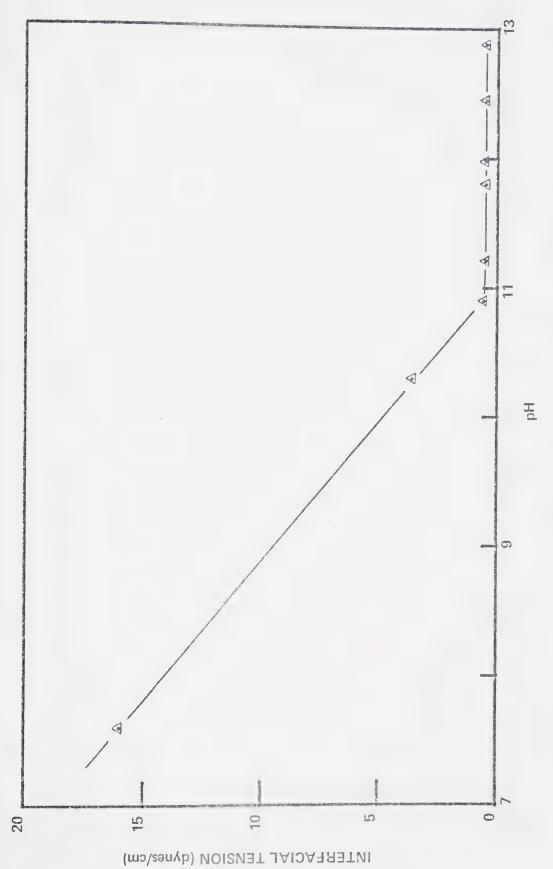


FIGURE A-5 INTERFACIAL TENSION AS A FUNCTION OF pH



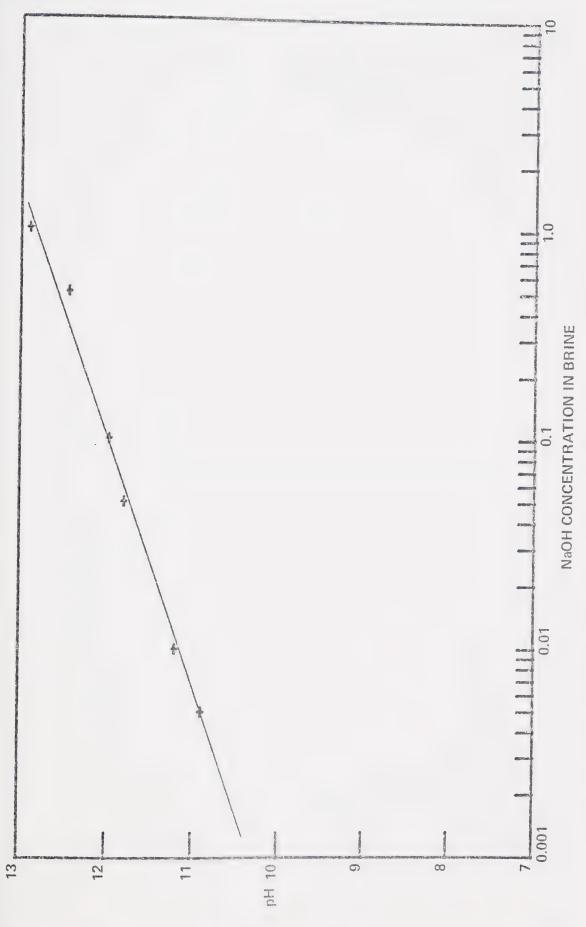


FIGURE A-6 pH AS A FUNCTION OF SODIUM HYDROXIDE CONCENTRATION IN BRINE



### APPENDIX B

SUMMARY OF THE SCALING COEFFICIENTS

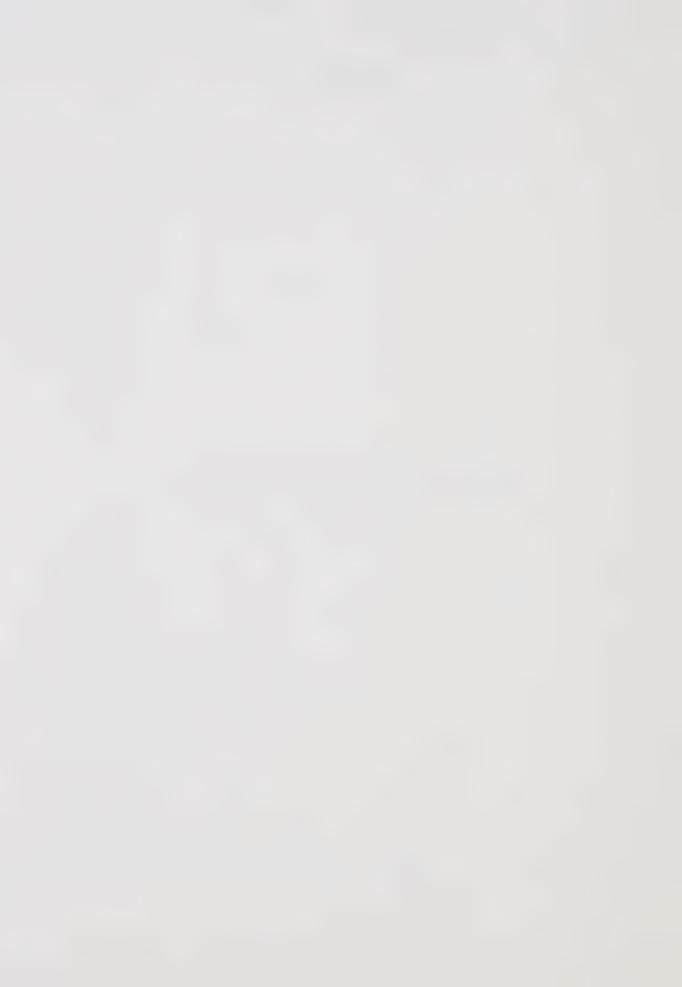


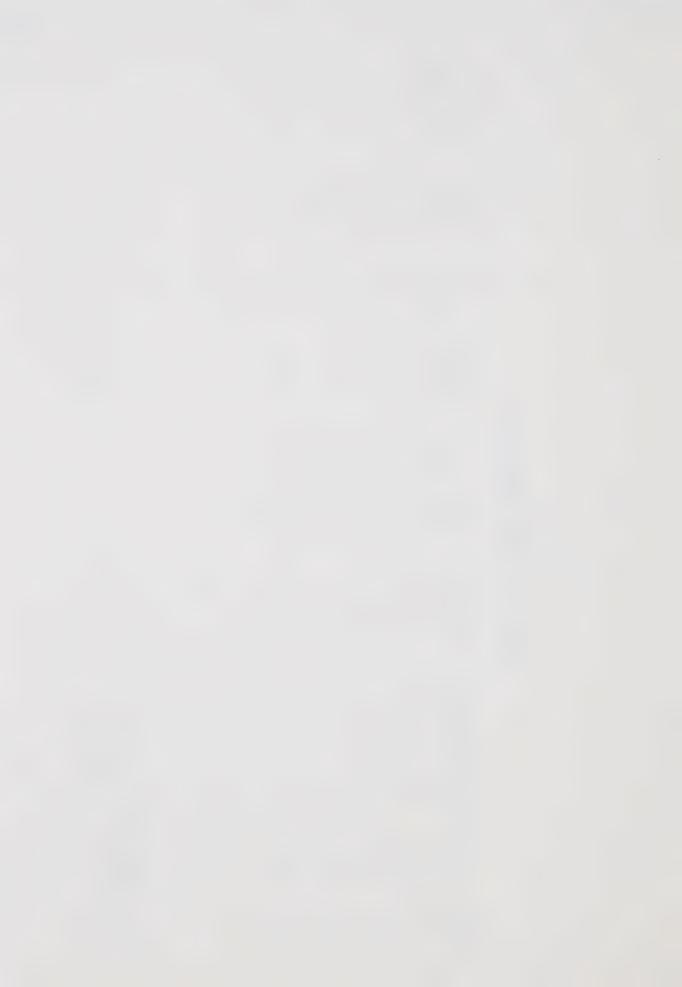
TABLE B-1

SUMMARY OF SCALING COEFFICIENTS

(3)	V(µ0-µW)	18.57	6.20	13.13	4.56	6.75
	T V K	0.04126	0.35761	0.08252	0.66020	0.35761
(1)	HWLV	0 0 0	33.13	7.65	61.20	33,15
K X10-8	cm2	et :- :- :- :- :- :- :- :- :- :- :- :- :-	37.43	37.43	37.43	37.43
	YOW	25.4	25.4	25.4	25.4	25.4
0,1	MI	778	805	778	805	629
Temperature	H 0	103.0	102.0	103.0	102.0	106.0
0. I.P.	WOR=10	47.5	0.65	48.8	52.0	51.0
rery % I.	T. WOR=6 WOR=1	Ç. 44.5	7°5°7	0.44	7.0	48.5
Recov	B.T.	16.7	19.9	14.9	18.0	19.5
Rate	cc/hr	09	260	120	096	520

Rapoport and Leas Scaling Coefficient de Haan Coefficient

Chuoke et al Coefficient. 365



## APPENDIX C

SUMMARY OF DISPLACEMENT TEST CONDITIONS

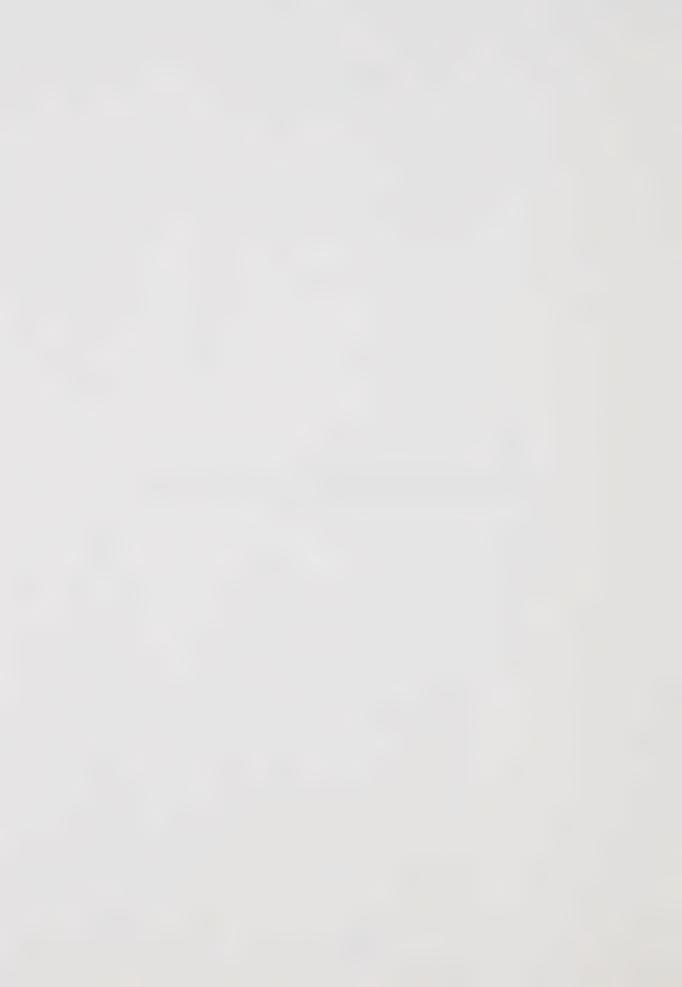


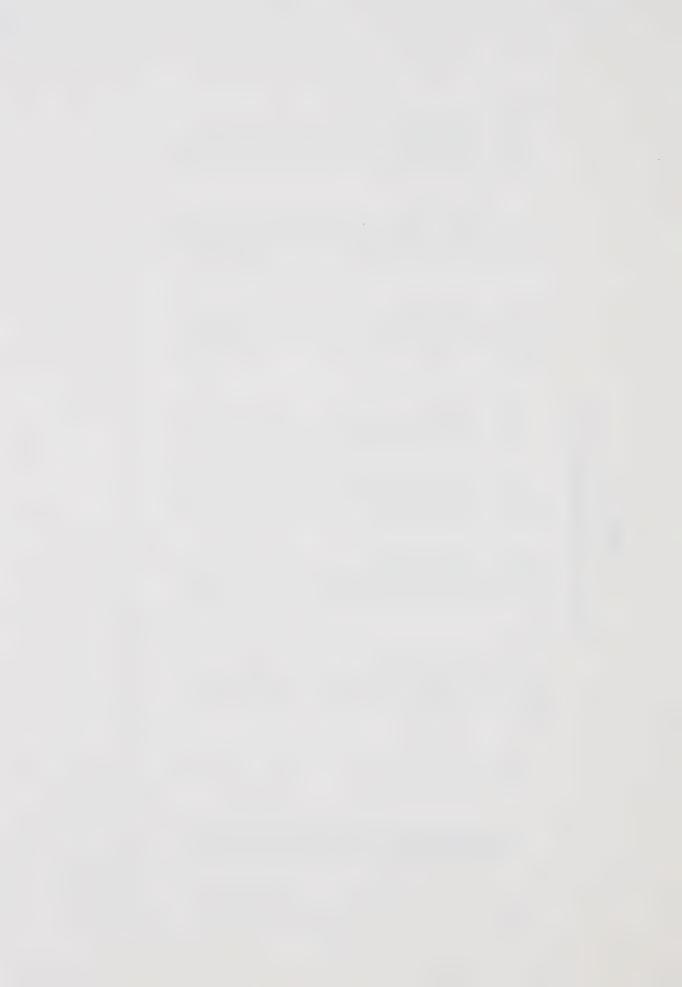
TABLE C-1

SUMMARY OF DISPLACEMENT TESTS

Pore Volume	594	594	594	594	778	730	830	830	762	669	820	703	727	809	812	805	749	801
NAOH % wt	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.005	1.000	0.100	0.100	0.100	0.100	0.100	0.100	1.000
Slug Size (cc)	* * * * * * * * * * * * * * * * * * * *	*******	表示於本次	*****	水水水水水	ペペペペペ	*****	****	عاد عاد عاد عاد	****	****	*****	250.0	325.0	280.0	105.0	402.0	105.0
K	37.73	37.73	37,73	37.73	27.22	24.59	28.37	28.37	27.00	27.68	27.47	21.82	26.46	24.50	22.46	24.50	21.82	22.65
ZMS	7.07	15.92	17.73	29.41	8.61	6.42	7.10	20.90	6.56	7.15	7.80	69.4	97.9	6.79	6.15	96.4	6.80	5.36
Rate cc/hr	560.0	120.0	0.096	0 000	320.0	320.0	320.0	480.0	320.0	320.0	320.0	320.0	320.0	320.0	320.0	320.0	320.0	320.0
Temperature °F	102.0	103.0	102.0	100.0	35.0	80.9	87.0	87.0	86.0	85.0	85.0	88.0	88.0	87.0	87.0	87.0	86.0	86.0
Sand		<del>-</del> 11		-	6-1	2	2	2	2	2	2	2	2	2	2	2	2	2
Run	1001	1003	1004	1005	2001	2002	2003	2004	3001	3002	3003	3004	4001	4002	4003	4004	4005	9005
Test	НС	1 M	†7	עו	9	7	$\infty$	6	10	11	12	13	14	15	16	17	18	19

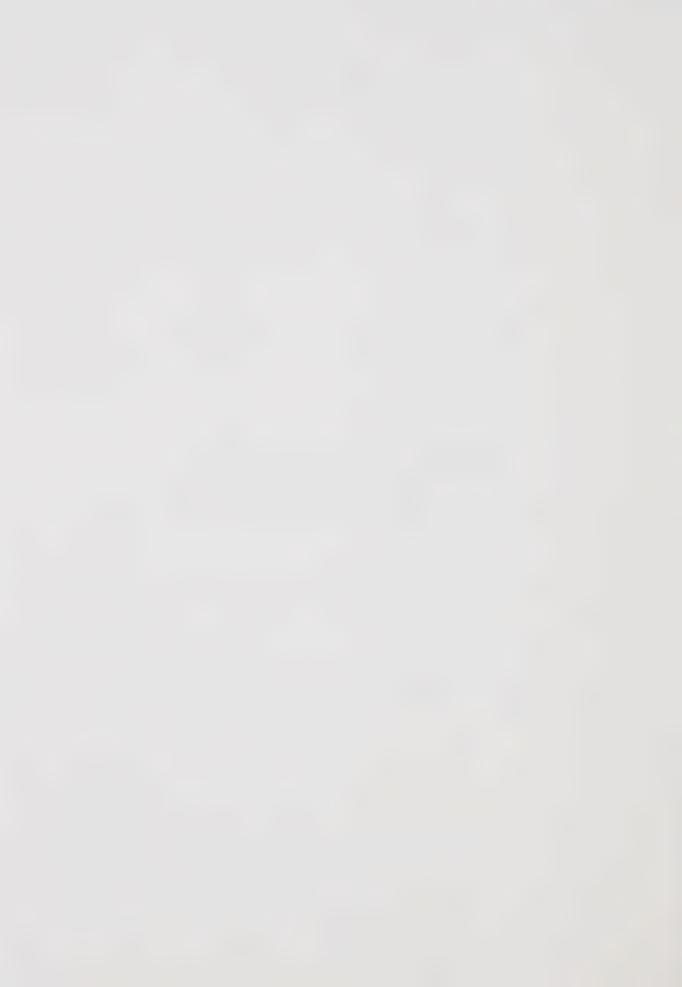
\*\*\*\* Sodium hydroxide added to the injected brine (infinite slug size)

\* Sand 1 = Golpher Sand 2 = Sparky



#### APPENDIX D

SUMMARY OF DATA FROM INDIVIDUAL
DISPLACEMENT TESTS



#### LIST OF SYMBOLS USED IN TABLE D

DWP Water produced during time step

WP Cumulative produced water

DNP Oil produced during time step

NP Cumulative oil produced

PIOP Percent initial oil-in-place

WI (CC) Cumulative water injected

(cubic centimeters)

WI (PV) Cumulative water injected

(pore volumes)

DP (PSI) Differential pressure across

core (PSI)

PV Pore volume

IOIP Initial oil-in-place

SWI Initial water saturation

\*\*\* Not measurable



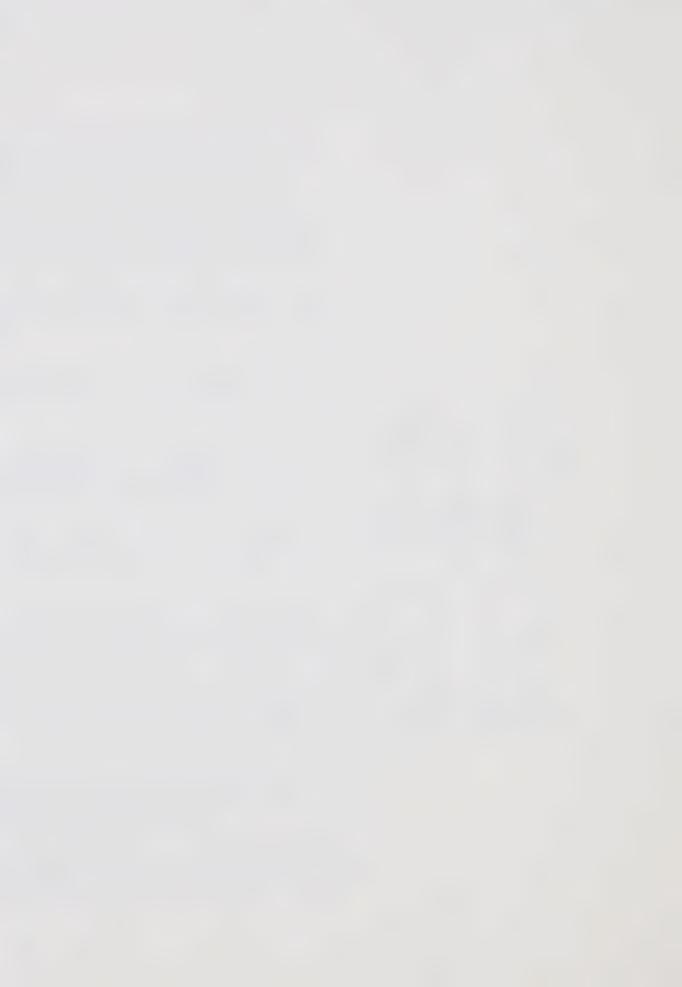
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RFFS F HR CENT NADH CYS	19.9275	WI (PV)	C		.2	0.28	(1)	4,		9.	9.	~	α •	6.	0	0		~	*	4.	
TABLE 00 DFG 00 CC/I 00 PER 00 CC	51 PV	WI(CC)				- 8				- 8		454.00				-				_	889.60
1 102.0 560.0 594.0 594.0 37.7 32.4	0.18	PIOP	9.6	8	-	5.3	9.7	2.1	4.6	5.2	7.8	39.29	1.0	2.2	3.3	4.4	5.9	7.3	3.6	9.4	2
ATURF = 12E TZE = 1ZE TRATION= = BILITY = TY = SCOSITY=	10 .00 CC	NP(CC)	2.0	•	•	145.70	.+		٠				.0	•		. 0	~			-	
RUN TEMPER RATE SLUG S CONCEN PV IOIP PERMEA SWI POROSI		DNP(CC	52.00	$\alpha$	0	5		е М	3	6.00						5.90		7.50		4.20	4.50
	THROUGH	WP(CC)	00.0		•	-	2	w W	19.	56.	• 96		6/	19.	59.	98.	36.	84.	24.	999	-
	BREAK	DWP (CC)	00.0					00.	.50	50	80	50	00.	8	00.	10	20	. 50	00	33	50

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			I							PERCENT	WOR	0.00	0			-	5	-	63	0	2.	0	7.	2	4.	4	5	ω.	11.66	
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2	0.0	茶茶茶	0.	0.46	501.7	7.7	5.5	2.4	5.0	0.14	PIOP			ω.	23.97	$\infty$	-	0	3	3	5	3	1.7	3.2	4.7	5.6	46.57	7.1	7.7	
1003	TURE =	2E =	$\alpha$	t design of the second	8 0 0	SILITY =	Range of the second		SCUSITY=	34.07 CC	NP(CC)	52.00				• +7			2 •	2.	3	2	6	-	۰ +	6	233.69	9	6	0 p
RUN	TEMPERA RATE	-1	UNCE	>		ш	3		IL VI	11	Z	52.00	2.	5.	$\subset$	4.	9	6		6	-			7.50				2.70		2.00
										THROUGH	WP(CC)				22.70			94.	21.	5 1.	77.	14.	47.	9 6°	34.		-	30 •	65°	90.
										BREAK	Ω_	00.0		9	-	91	υ.	R . C	7.30	0.20	5.80	6.80	3.00	6.00	8.00	4.20	8.50	3.80	2.00	2.00

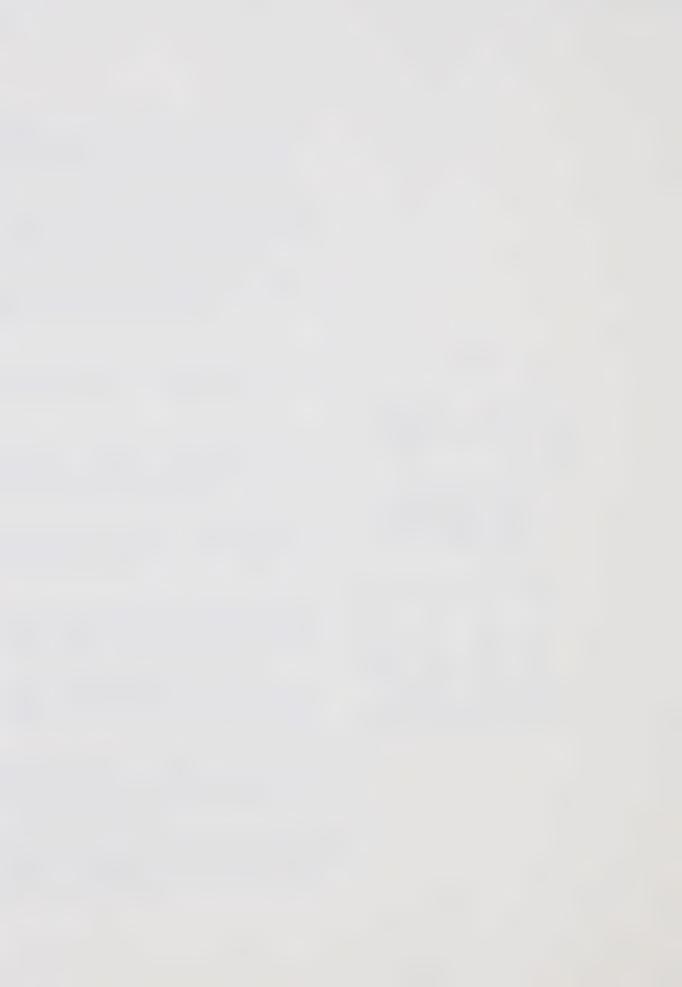
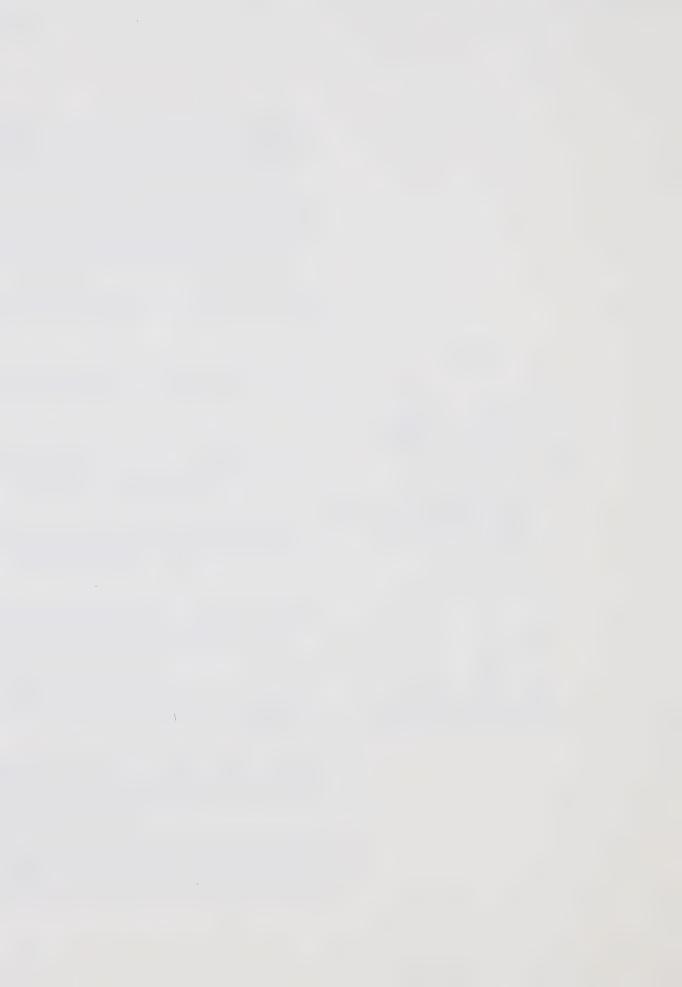


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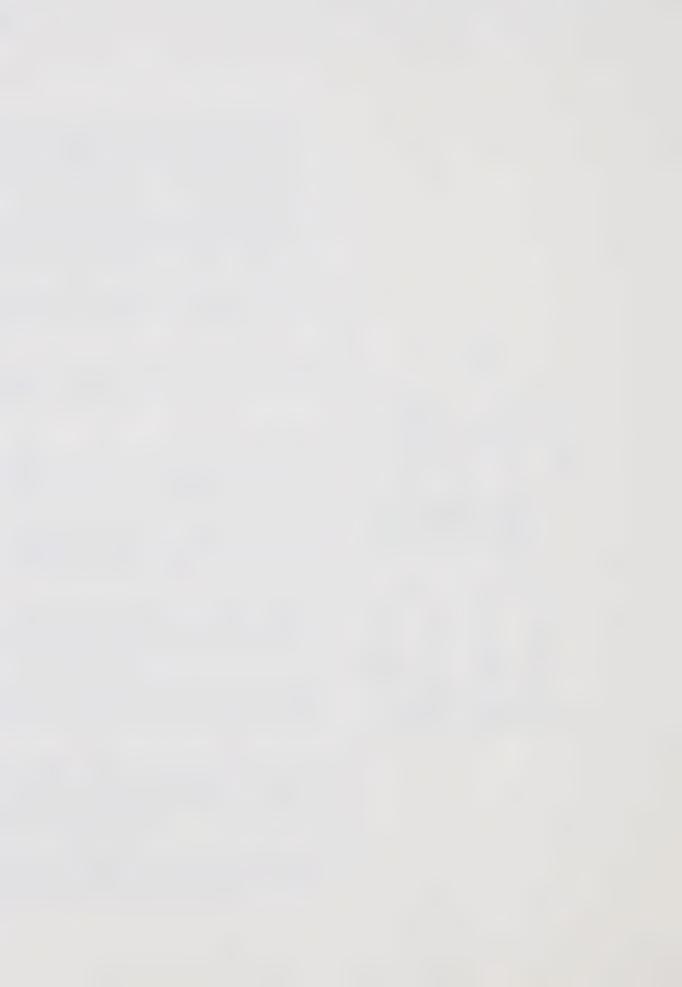
SLUG SIZE =** CONCENTRATION= PV IOIP PERMEABILITY = SWI	120.000 = 120.000 = 594.000 = 499.400 = 37.731	CC/HR CC/HR CC/HR PERCENT NACCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	NAOH
FE 11		PERCENT	
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PERCENT	MUR	0.00	00.00		0.07	0.33	0.41	0.86	1.30	1.90	2.66	3.22	3.91	3.85	4.68	5.53	6.00	7.09	7.65	7.22	00.6	11,000
14.9379	WI (PV)	0.00	0.06	0.11	0.14	0.15	0.17	0.25	0.32	0.40	0.50		0.68	0.70	0.78	0.86	0.93	1.01	1.08	1.17	1.24	1.28
55 PV	WI (CC)		41.50	68.10	84.10	94.10	106.10	148.90	193.90	242.69	297.70	344.20	404.20	421.20	466.70	515.70	557.70	602.20	647.20	698.20	738.20	762.20
0.12	PIOP	06.0	· 33	13,63	6.6	18,12	9. B	• 4	28.33	31.69	34.70	36.90	39.34	40.04	41.64	43.15	44.35	5	5.4	7	5	8,9
74.60 CC	NP(CC)	4.50	41.50	68.10	83.00	09 06	00.66	121.99	141.50	æ	173.30	184.30	-	0	0	-	. +-	C		238.39	242.39	244.39
	DNP (CC)		7.		4			3	6	9	.00	1.00	2.20	• 50	00.	. 50	.00	. 50	. 20	• 20	00.	
AK THROUGH	_	00.0	-	0.00	1.10	3.60	-	9	-	+		0	~		an .	~	9	10	S	0	22	~
BRFAK	DWP(CC)		0.00		1.10			0	5	2.00		5.50	7.80	3.50	7.50	1.50	00.9	00.6	08.6	4.80	00.5	2.00



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	ERCENT		0.00				0.77			9	4.54	5.00		7.16		9.37	8.78	0	10.80	2
RFES F HR CFNT NAOH CYS CENT	8.1319 P	(P		0.15		5	0.31	3	• 4	• 5	• 6	7	1.		96.0	0.	1.13	5.		
DEG CC/ CC CC CC CC DAR PERI	pv 1	20	68.00	œ	00.500	•	187.80	10	9.9	9.	6.1	5.9	14.99	24.00	5.0	5.7	•	21.7	7.0	18.5
102.00 960.00 94444444444444448864488.64	0.1491	OP	8.5 3.9	18.37	1.20	7.69	33,10	7.91	1.96	3.72	5.52	7.16	8,43	9.65	0.88	1.86	2.83	3.7	1. 17	5.3
ERATURE = **  SIZE = **  ENTRATION= = EABILITY = SITY = VISCOSITY=	18.67 CC	<u>d</u> (	68.00	000	3	10	161.75	10	2	3	°.	•	2	2.6	3.6	3.4	3.1	5.6	267.64	270.44
TEMPERA RATE SLUG SI CONCENT PV IOIP PERMEAB SWI. POROSIT OIL VIS	8		26.00	-	3		9	n	6		8.79			6.00					5.00	
	THROUGH	0	00.0	0.	· 4	9.	0	5	80 . 5	15.5	55.5	95.5	38 • 3	R 1.3	27.3	72.3	13.6	59.1	13,1	48.1
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		DP(PSI	ميار ميار ميار ميار ميار ميار ميار ميار ميار ميار ميار ميار	25. 25. 25. 25. 25. 25. 25.	25. 25. 25. 25. 25. 25. 25.	والمرافع والم والمرافع والمرافع والمرافع والمرافع والمرافع والمرافع والمراف	والمراج المراج ا	مال والدول و	مي مي مي مي مي مي	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	· · · · · · · · · · · · · · · · · · ·	於於於於於於	** ** ** ** **	华 花 华 花 华 花	· · · · · · · · · · · · · · · · · · ·	****	****
Tr.	PERCENT	WUR	0.00	0.00		0.47	06.0	2.15	7.67	3.85	3.76	5.93	5.63	7.00	6.64	11.00	12.57
REES F HR CFNT NADH CYS CENT	9.556A	WI (PV)	0.07	0.13	- 6	0.19						0.71			0.92	1.02	1.12
0 DEG 0 CC/ 0 CC/ 0 CC 0 CC 1 DAR 2 PER	0 PV 1	WI (CC)	43,00	82.00	7.	$\boldsymbol{\vdash}$				- 44	376.70	422.50	464.30	496.30	548,30	608.30	665.30
106.0 520.0 520.0 6.0 6.0 7.4 87.7 87.7 87.7	0.138	PIOP	0.2	5	5.	25.28	•	5.44	8.46	0,85	3.95	5.52	7.03	7.98	9.	50.80	51,80
ERATURF = ***  SIZE = ***  ENTRATION=  EABILITY =  SITY =  VISCOSITY=	2.00 CE	NP(CC)	43.00	82.00	94.50	106.00	129.60	148.60	161.30	171.30	184.30	~	promet.	2) 1, 19	1.9	212,99	217.19
RIJN TEMPERATURI RATE SLUG SIZE CONCENTRATI PV INIP INIP PERMEABILI SWI PORROSITY OIL VISCOSI	œ II	UNP(CC)	43.00		. 50	. 50	. 60	00.	64.	00.	.00	.59	• 29	00.	.80	00.	• 20
	THROUGH	MP(CC)	00.0			α.	29.90		04.	43.	92.	231.60	67.	95.	• 04	95.	48.
·	BRFAK	DWP (CC)	00.0			rU.	-		4.00	8.50	00.6	. 20	5.50	8.00	5.20	5.00	2.80



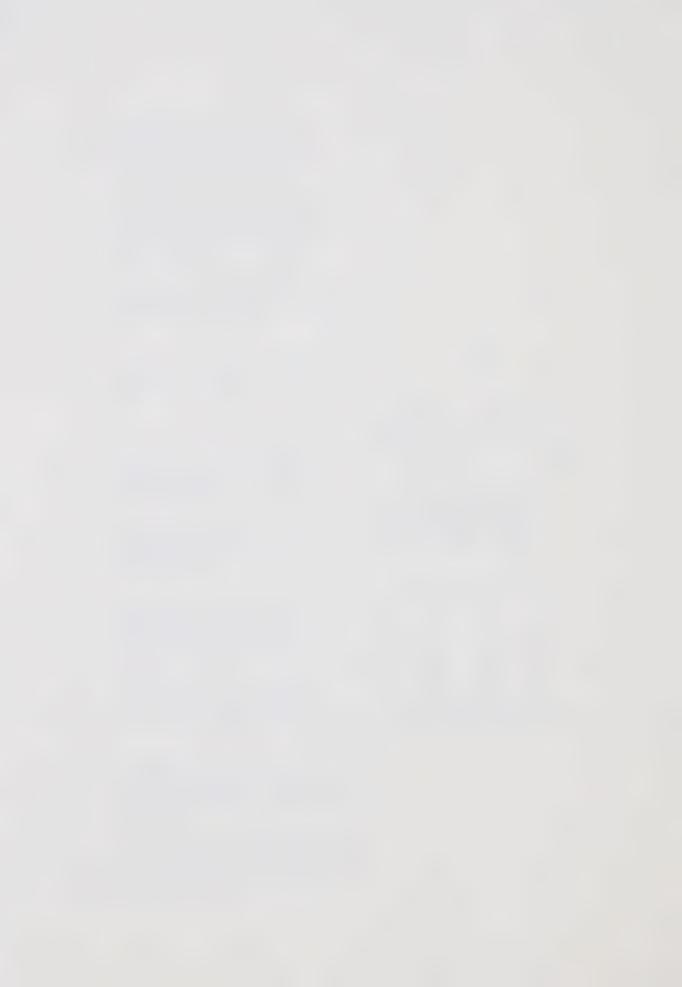
		ī			NANH						
IABLE DO		DEGRFFS	CC/HR	20	PERCENT	. 22	20	DARCYS	PERCFNT	PERCENT	СР
		85.000	320,000	11 安全 华 朱 朱 朱 朱 宋 宋 宋 宋 宋 宋 宋 宋 宋 宋 宋 宋 宋 宋 宋	0.000	778.000	711,000	27.225	8.611	41.651	1105,000
	RUN 2001	TEMPERATURE =	RATE =	SLUG SIZE =*	CONCENTRATION=	ρV	IOIP	PERMEABILITY =		PORUSITY =	OIL VISCOSITY=

	Н	· · · · · · · · · · · · · · · · · · ·	10 10 10 10 10 10 10 10 10 10 10 10 10 1	なななななな	40 10 10 10 10 10 10 10 10 10 10 10 10 10	30 30 30 30	35	مهر مهر مهر مهر مهر مهر	\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	36	400000000000000000000000000000000000000			\$ 50 00 00 00 00 00 00 00 00 00 00 00 00	· ** ** ** ** ** ** ** ** ** ** ** ** **	オンナンナ
	NP (PSI)	00	00	7000	56.00 *	34 36 36		5.00	36 36 36 36 36 36 36 36 36 36 36 36 36 3		26.00 *	24.80 *	22.50 #	** ** ** ** ** **	مارد على عادد عادد عادد عادد مارد على عادد عادد عادد عادد	19,80 *
ERCENT	MUR	00.0	0.03	0.50	1.48	2.41	4.03	4.22	5.30	6.25	7.16	6.68	7.61	10.88	12.57	12.33
9.5639 P	WI(PV)	0.06	0.08	0.11	0.16	0.21	0.26	0.33	0.38	0.43	0.50	0.56	49.0	0.71	0.78	0.83
74 PV	WI(CC)	50.00	69.00	88.00	127.00	168.00	209.80	256.80	297.80	341.30	390.30	443.30	- 4	552.80	609,80	08.649
0.0874	PINP	7.03	9.60	11.37	13.58	15.27	16.44	17.70	18,62	19.46	20.30	21.27	22.19	22.82	23,41	23.83
22 (0.89	NP(CC)	50.00	68.30	80.90	96.59	108.59	116.89	125.89	132.40	138,40	144.40	151.30	157.80	162.30	166.49	169.49
1 6	DNP (CC)	- 0				.00	. 29	.00	. 50	.00	00.	06.	. 50	. 50		3.00
BREAK THROUGH	WP(CC)	0.00	0.70	7.10	30.40	59.40	95.90	130.90	165.40	20 2 . 90	245.90	292.00	341.50	390.50	443,30	480.30
BREAK	DWP (CC)	00.0	0.70	05.9	23,30	29.07	33.50			37.50					.80	00



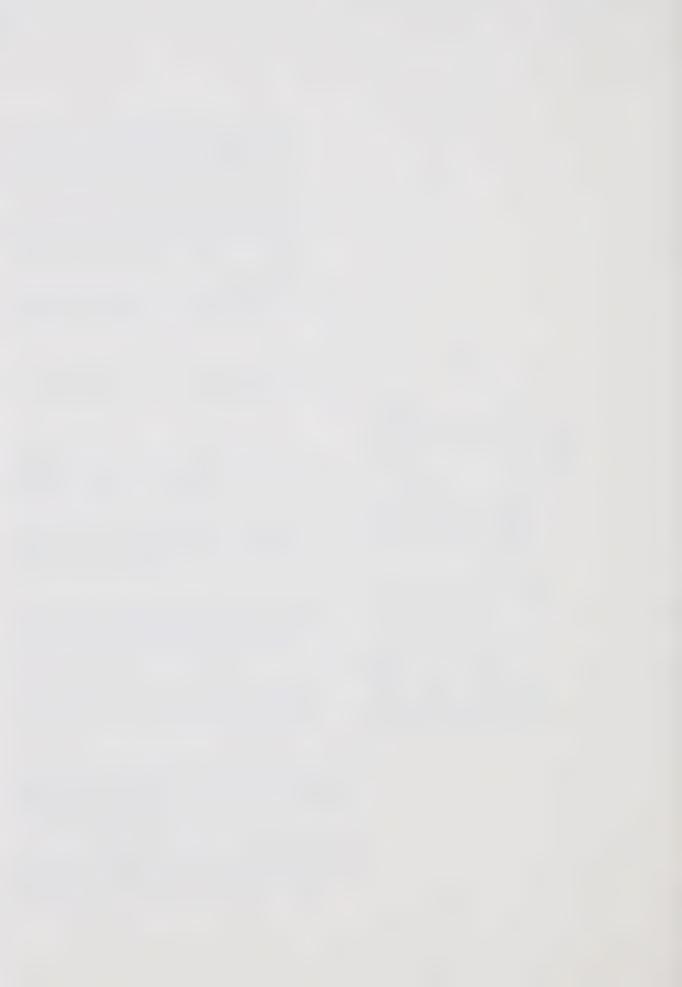
		u.			NANH						
TABLE N 7		DEGREES	CC/HR	CC	PERCFNT	22	20	DARCYS	PERCENT	PERCENT	СР
		86,900	320.000	· · · · · · · · · · · · · · · · · · ·	000.0	732,000	685.000	24.503	6.420	39.189	1105.000
	RUN 2002	TEMPERATURE =		SLUG SIZE =*	CONCENTRATION=	ρV	IOIP	PERMEABILITY =	IMS	POROSITY =	OIL VISCOSITY=

	ЬН	ななななななな	46 44 46 46	かかかからから	אר ילי ילי ילי ילי ילי ארי	16 16 15 16 16 16 18	35 35 35 36		35 35 35 35 35 35	مار مار مار مار مار مار	***	於本於於於於
	DP(PSI)	ما در	2 2 2 2 2 2 2 2	京 中 小 か か か か	65.00	49.00	42.50	3,4	مار مار مار مار مار مار	******	於水水水水水	* * * * * * * * * * * * * * * * * * * *
PERCENT	WUR	00.0	00.00	00.0	0.30	0.91	1,46	2.51	3.00	4.45	6.25	5.70
11.6788	WI (PV)	0.05		0.11	0.13	0.19	0.26	0.33	0.38	0.46	0.50	0.58
0.1092 PV	WI (CC)	38.00	70.00	84.00	00.66	143.00	193.50	247,30	-	343.30	372.30	429,30
0.10	PIOP	5.54	10.21	12.24	13.92	17.28	20.27	22.51	23.82	25.43	26.01	27.25
80 .00 CC	) NP(CC)	38.00	70.00	83.90	95.40	118.40	138,90	154.20	163,20	174.20	178.20	186.70
II.	DNP (CC)	38.00	_	_		_	_	15.29	_	-		_
BREAK THROUGH	(DD) dH	00.0	0.00	0.10	3.69	24.60	54.60	93.10	120.10	169.10	194.10	242.60
BREAK	DWP (CC)	0.00	00.0	0.10	3.50	21.00	30.00	38.50	27.00		00.	48.50



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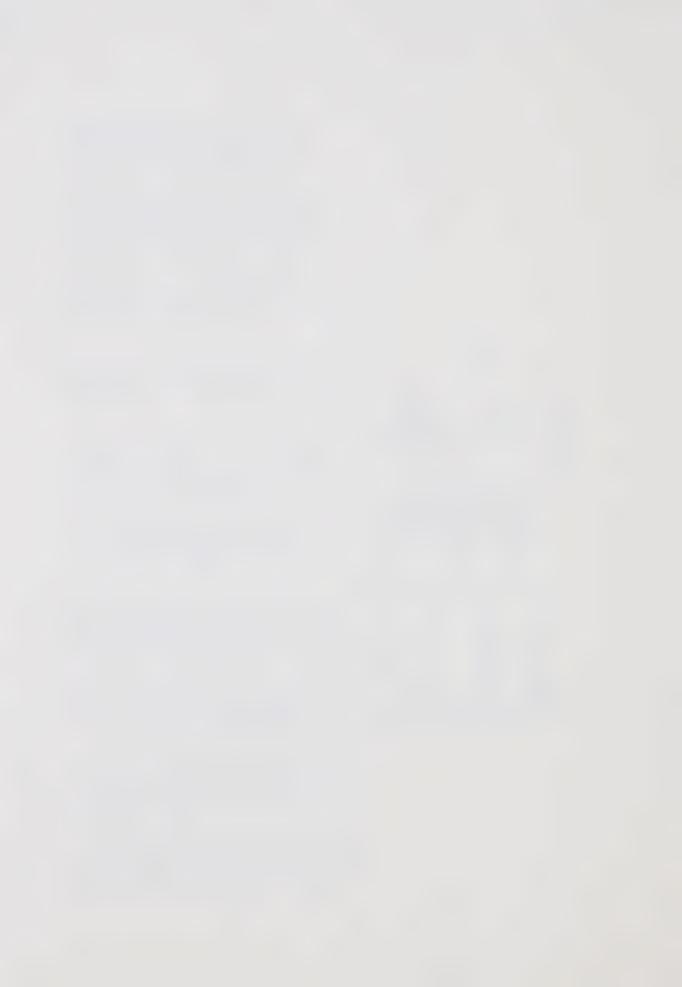
		Z =	2003		1 2 2 2 -				
		TEMPER	PERATURE =	87.		EGREFS F			
		ATE	0.00	320,000		HR			
		S SAT	12E =*	***	))				
		UNCEN	TRATION=	C	00 P	CENT NACH	H		
		>		30.0	00				
		d I U	81		0			•	
		FRMEA	BILITY =	000	372 DAR	$\searrow$			
		1	11	0	9	CER			
		<b>ORUSI</b>	YT		5 P	Ш О			
		IL VI	SCUSITY=	1120.0	0 0 0				
BREAK · TI	THROUGH	11	76.00 00	0.09	15 PV	9.R573	PERCENT		
(CC) M	Separate	PICC	) NP(CC)	PIOP	WI(CC)	WI(PV)	SAN .	OP (PSI)	H d
00		7 .	47.00	60.9	47.00	0.05	0.00	35	** ** **
00.		5	62.00		2	9		** ** **	3000
00		4.	76.00	9.85		0.	00.00	75.00	35
00.	1.00	$\alpha$	• +	12,19	95.00	0.11	0.05	0	34 34 34 44 44 44 44 44 44 44 44 44 44 4
000	9	٦,	19.	4	135.20		5	- 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	36 36 36
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50) 6	٠,	8.50	41.	* U	. 4	0.25	2.52	43.00	36 36 36
.00 IO			51,9	9.7	3 . 1		$\overline{}$	200 200 200 200 200 200 200 200 200 200	· · · · · · · · · · · · · · · · · · ·
10. 10.	٠,		61.4	0.9	*	0.36	3.80	そうちゃかかん	****
50 15			168.79	•	) . l	0.39	2.53	32.50	· · · · · · · · · · · · · · · · · · ·
61 00	9	6×°/	176.69	5.9	6 .	74. O	5.06	36	ない ない かんない
50 23	9		184.69	3.9	454.49	0.51	5.43	於於於於於於	مال مال دال دال دال دال
, 80 ZR			190.09	4.6	9.1	0.56	1	25.20	· · · · · · · · · · · · · · · · · · ·
10 32	e prod 1		0.56	5.3	516.79	0.62	8.02	35	مياد ميد ميد ميد ميد ميد
80 35	•	3.20		5.7	53.7	0.66	.10.56	22.80	於於於於於於
00 40	.+ 1		4.2	26.49	.80	0.73	•	**	****
,00 45	m	5.00	209.29	7.1	662.79	62.0	. 8	茶茶茶	35 35 35 35 35 35 35 35 35 35 35 35 35 3
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									NP(PSI)	داره داره داره داره داره داره داره داره	160.00	**	82.00	74.00	24. 25. 25. 25. 25. 25. 25.		56.00	44.00	各學學學學者	39.00	9	*
								PERCFNT	MUR	0.00	2	49.0	1.56	2.34	3.70	3.66	4.53	-	4.40	6.63	. 4	7.66
6 (	GREES F /HR	CFNT NANH		CYS	1.1	CENT		8.8347	WI (PV)	0.04	0.09		0.20					74.0	0.50	0.55	09.0	0.65
TABLE		PER	) U	5	3	1 P	0	98 PV	WI (CC)	39.50		29.	170.80	3	256.30	63	348.30	w	3		3	541.30
	87.000 480.000 480.000	0.000		3		44.43	1120,00	0.069	PINP	6.01	1.0	5		9.77	29	3.12	4.11	5.17	5.94	6.77	53	28.22
2004	0 n n	RATION=	13	BILITY =	\$ E	== 	CUSITY=	58.00 66	NP(CC)	9	72.50	10,2,00		6	139.80	151,80	158,30	165.30	1	175.80	180 .80	185,30
N. N.	TEMPERATURE RATE SLUG SIZE	C >	INIP	ERMEA	3	DRU	DIL VISCO	11	DNP(CC)		3	6	• 9		•	2					-	4.50
								THROUGH	WP(CC)		φ Θ	7	2 •	79.	].6	60 •	. 06	26.	48.	84.	321.50	56.
								BREAK	DWP(CC)		0 8	0.6	U V	7.00	7 • 0 • 0	4.00	9.50	00.9	2.00	6.50	37.00	4.50



								ЬН	44 44 44 44 44 44 44	**	35	مياد ماد ماد ماد ماد ماد ماد ماد ماد ماد ماد ماد	* * * * * * * * * * * * * * * * * * *	200000000000000000000000000000000000000		なななななな	12.65	2.7	7.	300	12.80	상
						•		NP (PSI)	** ** ** **	* * * * *	· · · · · · · · · · · · · · · · · · ·	ないかいかかかか	260.00		140.00	ななない ないない	90.09	00.99	58.00			* * * * * * * * * * * * * * * * * * * *
		T					ERCENT	MOR	00.00		0.00	00.0			0.28	.5	6.	2.52	9.	5.36		62.9
UIU	REES F HR	ENT NADH		- X-	Z		9.9438 P	WI(PV)	00.00	0.05	7	-			0.30		0.41	0.49	0.54	0.59	0.66	69.0
TABLE	DEG CC/	P 0	20	5 DARC	PER	CP	3 PV 1	WI(CC)	4.00	40.20	82.70	~	142.50	*	235.09	3.6	9.6	9.6	14.10	+52.29	03.7	530.29
	86.000 320.000	1.00	• 00	7.00	.63	• 00	0.186	PINP	0.56	9.		. 93	.01	.21		.62	• 66	• 05	.17	.02	3.0	43,55 5
3001	TE:	TRATION=	}		>-	SCOSITY=	142.00 CC	NP(CC)	4.00	40.20	82.70	27.	2	<b>7.</b> 6	+ .	4		285,19			9.90	310.09
RUN	MP ER TE UG S	CEN	0 2	SWI	PURUSIT	/ I	14	DNP (CC)	4.	9	2	45.00	<b>5</b>	_	42.00	25.00		_	9	00.9	7.50	3.40
							THROUGH	MP(CC)	0.00			00.0		* 	13.67	. (	• x	91.	$\sim$ 1	53.		220 • 19
							BREAK	DWP (CC)	00.0	0	0	0	٠ •		ω ι	υ. υ.	( • (	5.00	9.50	7.20	4.00	3.10



	· .	PSI) PH	.00	ما ما ما ما ما ما ما ما ما	かかかかかから かかか	大学 子子子 大学	· 00 *****	36.00 ****	· · · · · · · · · · · · · · · · · · ·	3,0	30 30 30	* *	مي مي مي مي مي مي	******* 00	*****	* * * * * * * * * * * * * * * * * * * *
		0) dU	210	水水水水	35. 35.	かかかか	38	36	300	29	ななれ	本本本本	ながれた	3	22.	3,6
Ξ	PERCENT	WOR	00.00	0.02	2.13	3.55	4.10	5.28	5.00	7.55	5.06	7.60	7.77	10.77	13.66	10.11
SREES F HR CENT NADH CYS CPNT	6060°6	WI(PV)	0.04			~	ζ.		0.44	5	5	9.	7	1		0.91
TABLE  O DEGI  O CC/P  S PERC  O CC  O CC	) y d	WI(CC)	9.8	68.0	7 .	3	06.603	3	310,30	• 4	4,	4.	0	0	00.06	37.79
85.00 320.00 ******* 0.00 699.00 649.00 27.68 7.15	0.084	0 P	5	.32	. 52	90.	.60	.68	18.15	.87	040	.17	.86	. 55	, 02	68
BEATURE = \$3002 SIZE = \$\times\$ ENTRATION = \$\times\$ EABILITY = \$\times\$ VISCOSITY = \$\times\$	00.6	-	29.80		-Ch				117.79					46.	9.4	5
RUN TEMPERATI RATE SLUG SIZ CONCENTR PV INIP PERMEABII SWI PORNSITY		DNP (CC)			8					-			4.50			4.29
	K. THROUGH		0.00	٠.	51.50	-	ω Ωι	٠ د	746.50	r c	m.	٠ ب		ر پ	•	·+
	BREAK	α.		0					47.00							



		ŭ.			NADH						
TABLE D12		DEGREES	CC/HR	CC	PERCFNT NACH	CC	CC	DARCYS	PERCENT	PERCENT	CP
		85.000	320,000	********	1.000	820.000	756.000	27.475	7.804	43.900	1105.000
	3003	TEMPERATURE =	88		CUNCENTRATION=	13	13	PERMEABILITY =	11		OIL VISCOSITY=
	RUN	TEMPER	RATE	SLUG SIZE	CUNCER	ΡV	IOIP	PFRME	IMS	PURUSITY	OIL VI

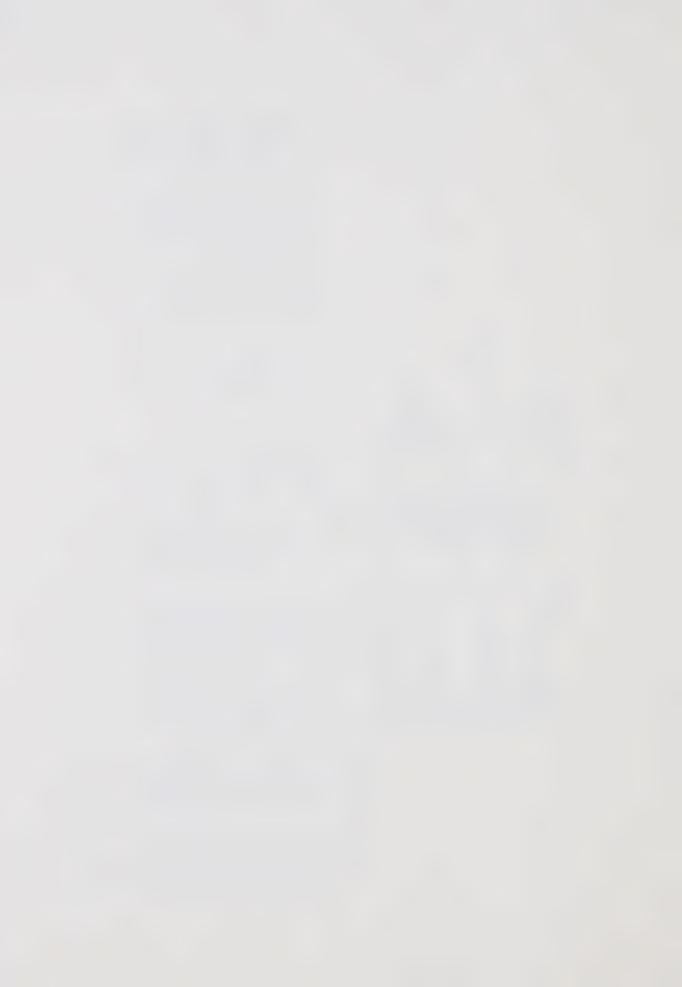
	Hd	مار مار مار مار مار مار مار	3,0	30	300000000000000000000000000000000000000	35	30		4,0	, mail	12,75	なかないなか	-	a	35 35	12.89
	NP (PSI)	236.00	***	233.00	173.00	於 · · · · · · · · · · · · · · · · · · ·	146.00	111.00	30 00 00 00 00 00	84.00	76.00	61.00	******	42.00	40.00	****
PERCENT	MUR	00.00	0.00	00.00	00.0	0.05	0.20	0.22	1.00	1.68	2.54	2.57	5.25	10.90	8.68	12,74
22.7248 F	WI(PV)	0.05	0.09	0.15	0.20	0.22	0.25	0.30	0.35	0.41	0.46	0.50	0.60	79.0	0.71	0.77
195 PV	WI(CC)	41.00	80.80	126.80	171.80	186.80	207.80	250.80	290.80	337.80	380.30	417.80	492.80	552.30	589.10	633.10
0.2095	PIOP	5.42	10.68	16,77	22.72	24.60	26.91	31.54	34.19	36.50	38.09	39.48	41.07	41.73	42.23	2.6
171.87 CC	Z	41.00	80 .80	126.80	171.80	186.00	203.50	238.50	258.50	276.00	288.00	298.50	310.50	315.50	319,30	322,49
	) DNP (CC)	41,10	39.80	46.00	45.00	14.20	17.50	35.00	20.00	17.50	12.00	10.50	12.00	5.00	3.79	3.20
BREAK THROUGH	VIP (CC)	0.00			00	80)		3	30	61.80			30	236.80	30	5
BREAK	DWP(CC)	00.0	00.0	00.0	00.0	0 .80	3.50	8.00	20.00	29.50	30.50			54.50		



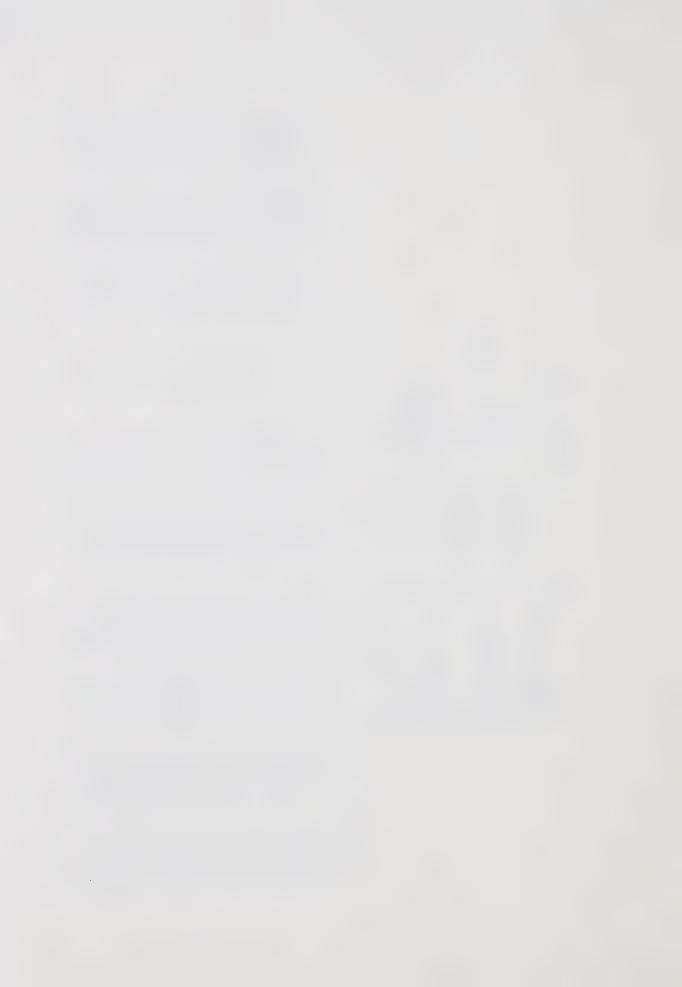
												Hd .	30 30 30 30 30 30 40	36	****	35		11.75	6.	11.92	30 30 30 30 30	11.98	· 水·	-	상
		*										()Sd)dU	350.00	264.00	183,00	155.00	124.00	ないない はなか	かき なかがか	41.00	42.00	60.44	45.00	44.00	44.00
				_							PERCENT	MOR	00.0	0.00	0.00	0.00	0.07	0.82	1.47	2.44	3.07	3,55	5,11	8.66	7.60
D13	DEGREES F	HR		CFNT NADH			>	CENT	****		25.4477	WI (PV)	0.06	0.12	0.19	0.24	0.28	0.35	0.41	0.48	0.55	9.	69.0	0.77	0.84
TABLE		/33		PER	$\mathcal{C}^{\mathcal{C}}$	00 00	27 DAR	94 PERCEN	9	<u>a</u>	5 PV	WI (CC)	43.00	89.00	135.50	170.50	200.50	247.10	294.10	340.60	393.60	434.60	489.60	547.60	290.60
	88.000	320.00	******	0.10	703.000	670.000	21.82	9.	38,40	0.0	0.242	PIOP		3.2	0.22	25.41	69.6	3.41	6.25	8.26	0.20	1.55	• 89	3.79	33
3004	ITURF =	11	312F = #	RATION=		11	SILITY =	davo speci		CUSITY=	170.50 CC	NP(CC)	43.00	89.00	135.50	170.30	198.30	223.90			269.40	278,40	287,40	293.40	298.40
RUN	TEMPER/	RATE	SLUG SI	CONCENT	ρV	INIP	PFRMEAE	IMS	POROSIT	OIL VIS	11	DNP (CC)	00*	00*9	6.50	4.80	8.00	5.60	00.6	3.50	3.00	.00°	00.	.00	00.
											THROUGH	MP(CC)		0.00		0.20	2	23.20	mad .	× .	+	0	(1)	254.2)	292.20
											BREAK	DWP (CC)	00.0			-	ζ,		8.00	3.00	00.0	2.00	00.9	00	00.8



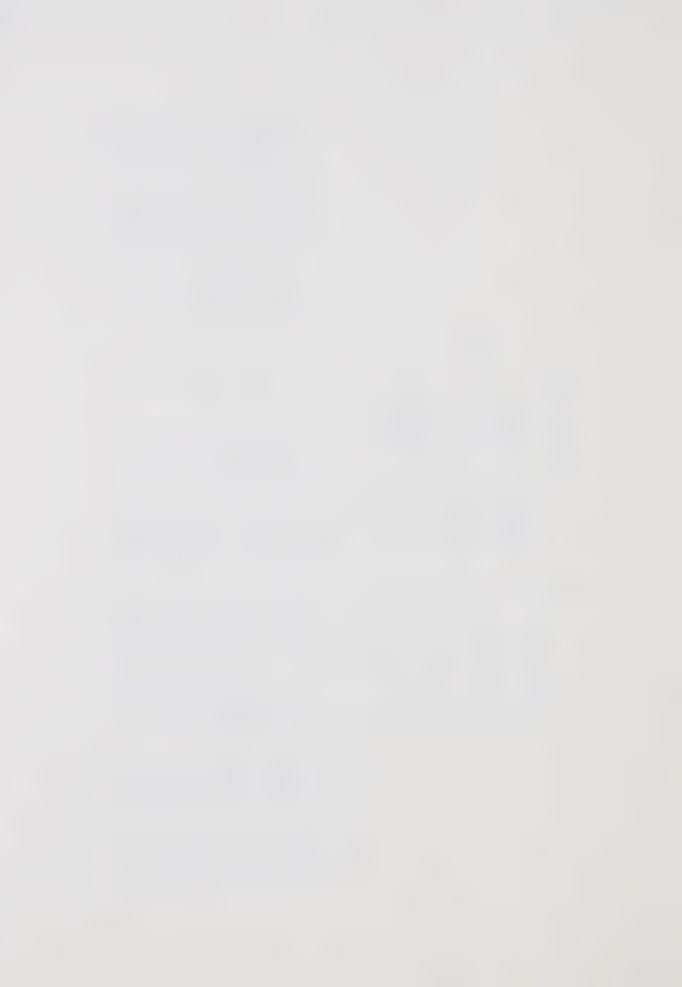
													ЬН		100 of 100 of 100 of	مار مار مار مار مار مار	からからかかかか	11.20	10.65	* * * * * * * * * *	林 於 於 於 於 於	9.91	** ** ** **
													np (PSI)	360.00	280.00	220.00	170.00	112.00	於於於於於於	60.64	32,00	26.00	22.00
					I							PERCENT	WOR	0.00	0.00	00.00	0.00	0 • 40	3.05	4.47	5.00	10.20	20.00
D]4		DEGREES F	HR		CFNT NADH			CYS	FRCFNT	CENT		25.2941	WI(PV)	0.06	0.13	0.20	0.23	0.30	0.36	0.43	0.51	• 5	0.65
TABLE			OC CC/HR		PER	22 00		DAR	Q.	0	. CP .	65 PV	WI(CC)		99.50	149.50	172.00	221.00	268.80	315,30	375.30	431,30	473.30
		88.000	320,000	250,000	0.100	727.00	680,000	26.414	497.9	30.1	00.066	0.236	PINP	7.13	14.63	98		44	17	45	89	53	35.92
	4001	APERATURE =	11	= 3218 S	FRATION=	21	11	ABILITY =	11	 	SCUSITY=	172.00 CC	NP(CC)	48.50	04.66	149.50	172.00	207.00	218.80	227.30	237.30	242.30	244.30
	RUN	TEMPER /	RATE	SLUG SI	CONCENT	ΡV	IUIP	M	IMS	PORUSITY	OIL VISCO	11	ONP (CC)	48.50			22.50					5.00	2.00
												BREAK THROUGH	MP(CC)	0.00	00.0	0.00	00.0	14.00	50.00	88.00	138.00	0	229.00
												BREAK	DWP (CC)	00.0	00.0	0	00.0	14.00	36.00	0		0	40 • 00



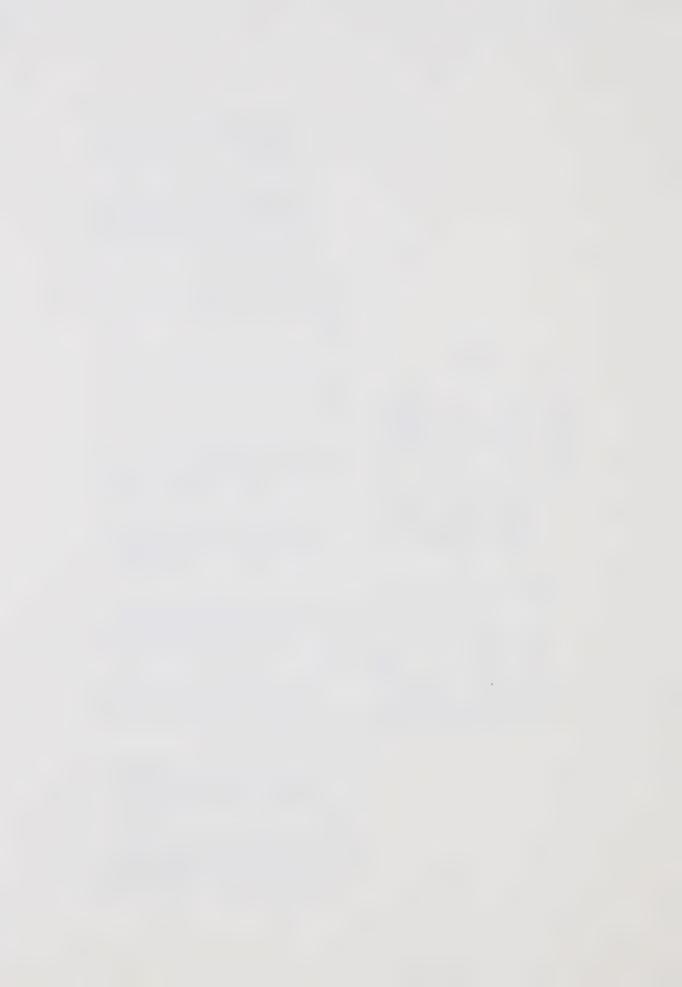
		± 199							Hd .	********	10 10 10 10 10 10 10 10 10 10 10 10 10 1	***	から かかかか	$\overline{}$		_	1	35	11,30	华		オントナナンオ	06 * 6
				,					(ISA) dU	50	93.50	35	本なななな	90.09	00.46	かかかかかかかか	98.00	مار جال جال مال جال جال جال جار جال جال جال جال جال	70.00	华	38.00	5	* * * * * * * * * * * * * * * * * * * *
		7						ERCENT	WUR	0.00	00.0	00.0		3	~	30	0	-	1.82	$\infty$	3	0	7.84
N15	RFES F HR	CFNT NADH		CYS	Z	CFNT		20.2917 P	WI(PV)		-	. 0.17		0.	00	~	. +	. +	10	10	0.65	2-	0.77
TABLE	neg CC/	7 0 0 8 0 0	0	3 DAR	8 PER	1 PER		1 PV	WI (CC)		90.50	38.5	57.		51.	93.	34.	80.	420.00	75.5	33.	$\propto$	626.00
	87.000 320.000	0 0	7	4.5	10	43.31	1020,00	0.189	PINP	•	2.0	6	0	5.3	8.7	1.7	4.5	7.3	6	1.1	2.5	3.5	44.24
4002	# H H H	TRATION=	88	ILITY		II	COSITY=	3.00 CC	NP(CC)	46.50	90.50	138.50	S.	91.	216.70	39.	260.70	281.70	295.70	-	20 •	28.3	333.59
RUN	E.R.	ONCEN V		PERMEAB		NRUSI		= 15	DNP (CC)	46.50		48.00		- 8					14.00				
								BREAK.THROUGH	MP(CC)	0	00.0	00.0	1.00	5	4	3	3	æ	124.30	65.	2	51.	6
								BREAK	DWP (CC)	0.00	0		0	4.0	9 . 8	0.6	0.0	5.0	25.50	1.00	08.9	9.50	0 * 80



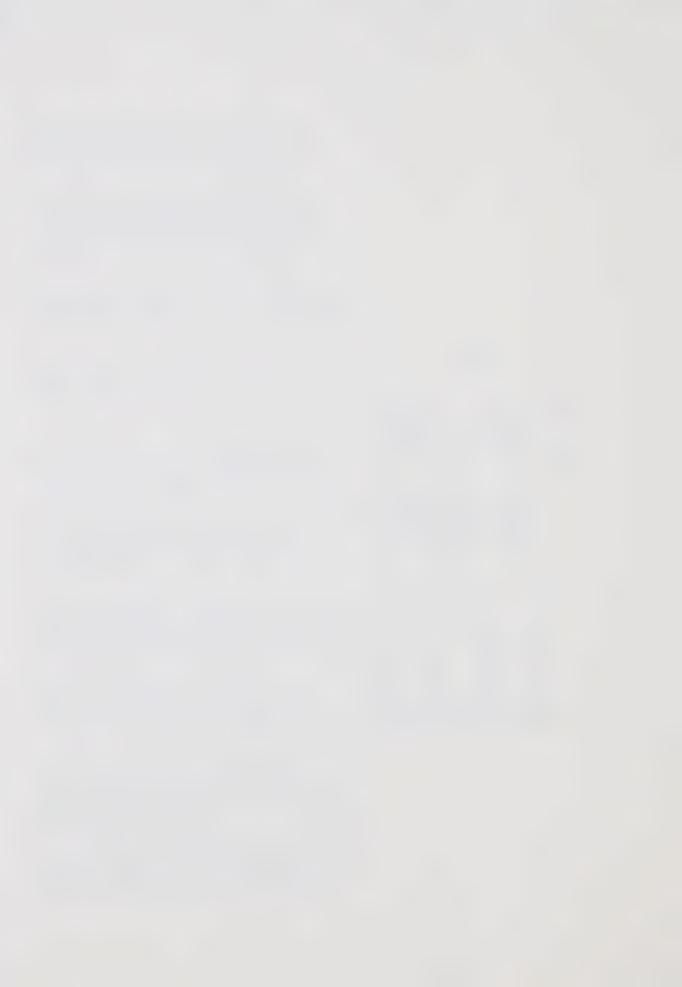
		PH PH ********************************
		DP (PSI) 340。00 ******** 240。00 170。00 ******* 75。00 ********
	ERCENT	MUR 0.00 0.00 0.00 0.00 0.00 0.33 1.28 2.46 5.00 7.26
BLE D16 DEGREFS F CC/HR CC	24.6719 PI	W1 (PV) 0.05 0.11 0.17 0.22 0.25 0.31 0.35 0.45
T	5 PV	WI (CC) 46.00 92.00 139.00 207.00 259.00 259.00 259.00 428.00
87.000 320.000 280.000 0.100 812.000 762.000 22.461 6.157 43.472	0.2319	PINP 6.03 12.07 18.24 18.24 18.24 127.03 232.15 232.15 233.98 235.69 336.35 37.86 4
RUN 4003  FMPERATURE = ATE LUG SIZE = ONCENTRATION= ON P = ERMEARILITY = ON P =	88.00 CC	NP(CC) 46.00 92.00 139.00 206.00 2075.00 275.00 277.00 284.50
RUN TEMPERA RATE SLUG SI CONCENT PV IOIP PERMEAP SWI PORDSIT	· ·	DNP (CC) 46.00 46.00 47.00 45.00 22.00 39.00 13.00 5.00 7.50
	THROUGH	WP (CC) 0.00 0.00 0.00 0.00 1.00 14.00 32.00 64.00 89.00
	BREAK	DWP(CC) 0.00 0.00 0.00 0.00 1.00 13.00 18.00 25.00 25.00



													Н	******	が かいかかかか	· · · · · · · · · · · · · · · · · · ·	9.65	9.08	***	8.85	36	8.78	なななななな	オネルドネ	8.75
													DP(PSI)	250.00	130,00	125.00	124.00	* * * * * * * *	46.00	*******	30.00	26.00	21.00	21.00	20.00
												PERCENT	WUR	00.0	00.00	0.01	0.43	1.02	1.69	3.54	9	9.54	5.21	11.14	7.23
. n17		RFES F	HR		CENT NACH			CYS	Z	CEN		15.5555	WI (PV)	C	0.12	-	~	0.27	3	0.37	0.43	5	0.55	0.60	19.0
TABLE		0	700 00	0		C	0	3 DAR	C.	7	0	8 PV	WI (CC)	51.00	104.00	130.50	176.50	223.00	271.00	302.80	.0	404.60	448.10		544.10
		87.00	320,000	105,000	0.100	0.5	765.00	24.50	0000	43.09	1020.00	0.147	PIOP	99.9	6	6	7	<u>~</u>		27.42	.+	5	_	33	31.38
	4004	ATURE =	\$ \$	SIZE =	TRATION=	17	88	BILITY =	2 m 8 8	11 1	SCUSI TY=	119.00 CC	(D) NP(CC)	51.00	104.00	130 .00	162.00	185.00	20 2 80	209.80	217,60	223.10	230.10	233.60	240.10
	RIIN	FMPER	Q	5117	CONCENTRAT	ρV		RMEA		<b>DR D S I</b>	IL VI	11	DNP(CC	51,00	3	26.00	2	3	_	7.00	7.79				6.50
												THROUGH	MP(CC)	00.00	00.0	0 • 20	14.50	38.00		93		181,50	218.00	257.00	30 4.00
												BREAK	DWP (CC)		00.00		14.00		-	24.80	00.	• 50	• 50	00.	00•



		Hd	** * * * * * *	<b>特</b> 特特 特特	於於於於於於		10.70	1.4	11.75		-			•	6	34	10.35	
		(ISd) du	350.00	274.00	06	74.	135.00	07.		100			- 6	59.00		50.00	0	31.00
<del>T</del>	PERCFNT	WOR	00.0				0.23	æ	r.	2	.5	6.	4.	0	0		5	
RFFS F HR CFNT NAOH CVS CENT	1.6045	HI (PV)	0.05			~	0.26	3	*	• 4	.5	• 5	• 6	9.	7.	0.79	00	06.0
TABLE  0	3 PV 2	WI (CC)	42.50	7.0	3	50.8	$\alpha$	38.3	81.	30.1	79.1	54.6	67.1	515.10	51.1	593.90	06.749	680.40
86.00 320.00 402.00 0.10 749.00 698.00 21.82 6.80 40.92	0.201	PIOP		2.	6,45	1.60	.71	0.08	5.49	4.64	49.9	B.29	9.6	1.3	2.6	44.14	5.8	46.79
4005  ATURE = 12E = 12E  TRATION = 12E = 1	50 .80 CC	NP(CC)	42.50	87	35.	50.		10 .	26.	+	55.	57.	16.	288.80	297.80	98.	320.10	326.60
RUN RATE SLUG SIZE CONCENTRATI PV IOIP PERMEABILIT SWI POROSITY	11	Z	42.50	• +	œ	2	٠ د د	3	16.80	5	4.	•	6		00.6		2	6 • 50
	THROUGH	MP(CC)	0.00					о С		x (	23.	57.	, (v)	26.	53.	85.	7	53.
	BREAK	<u>D</u>	00.0	0	0	° ا	• (D	0 (	0 (	00.	00.	00.	00.	00.	00.	. 50	00.	00



													Hd	35 35 35 35 35 35 35 35 35 35 35 35 35 3	さんかい かいかい	****	於於於於於於	11.55	11.35	11.10	オオポポオオ	10.92	**	10.50	35
													(ISA) dU	335.00	40	158.00	150.00	****	والمراجع والم والمراجع والمراجع والمراجع والمراجع والمراجع والمراجع والمراج	105.00	80.00	78.00	68.00	0	44.00
				22 000	<b>T</b>		58.000 C			PERCE	5.000 CP	PERCENT	WOR	00.00	0.00	00.0		0.80		1.87					5.50
N19		RFFS F	T.		CENT NADH			いとい	ban			17.5461	WI (PV)	0.	0.11	•	5	3		0.45	4.		• 6	79.0	0.73
TABLE			700 000		FX			DAR	PER			0 PV	WI (CC)	47.50	95.00	130.00	181,00	246.00	13.	360.50	98.	47.	0	540.00	592.00
	,	86.000	Ċ	05.	$\bigcirc$			22.6	6	œ		0.166	PINP	.2	2.5	17,15	2.9	7.	•	34.10	5	7.	6	6.6	41.02
RUM 4006	4005	TURF =	H	= ∃Z.	RATION=	dis-o		SILITY =	83	POROSITY	IL VI	33.00 66	NP(CC)	47.50	95.00	137.00	174.00	210.00	242.00	258.50	269.50	283.50	296.00	30 3 .00	311,00
						>		Ш	3			11	DNP (CC)			2.00	4.00	00.9	2.00	6.50	1.00	4.00	2.50	00.	•00
												THROUGH	WP(CC)	00.0	•		7		Ţ,	102.00	9	4.0	3.0	237.00	1.0
												BREAK	DWP (CC)	0.		0	~	0.6	5.00	C	7.00	2.00	00.6	4.00	00•



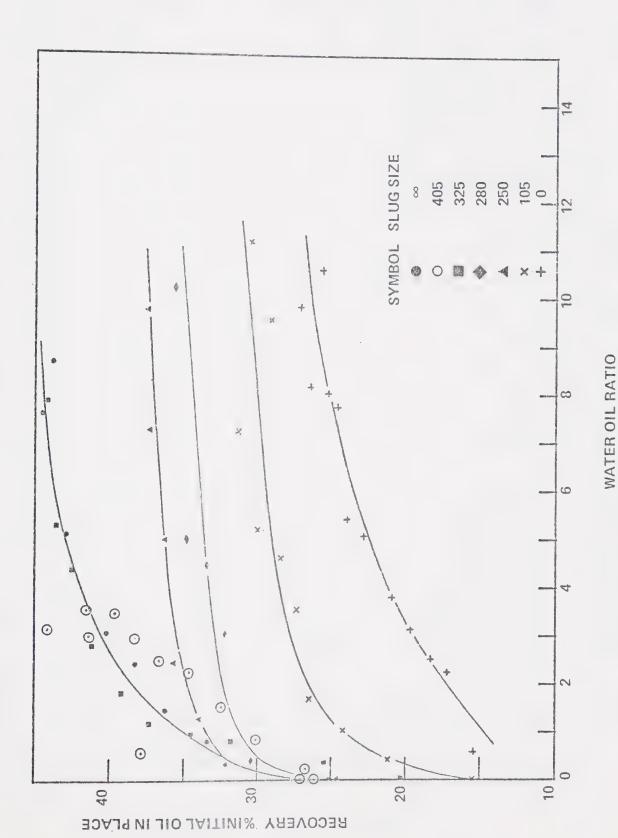
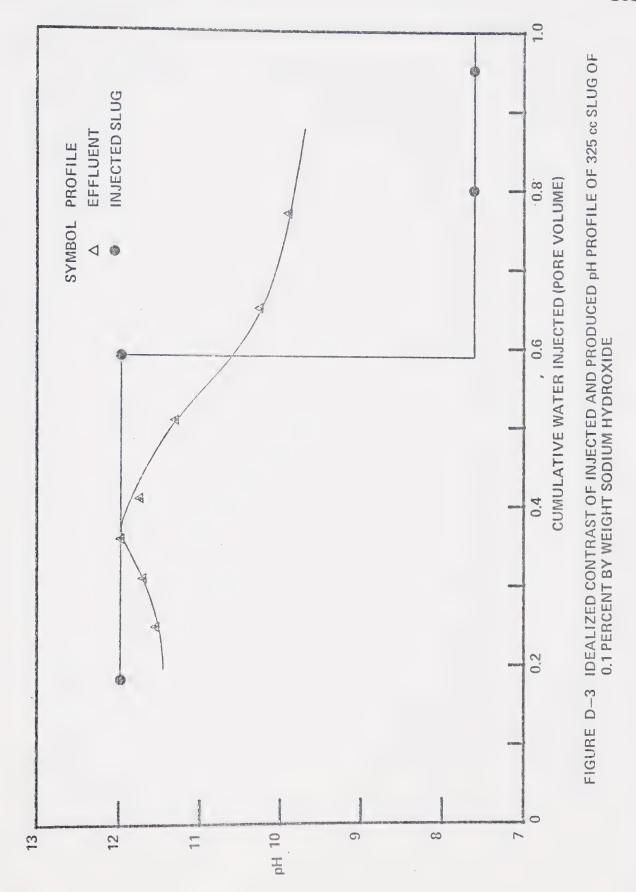


FIGURE D-1 RECOVERY AS A FUNCTION OF WATER OIL RATIO FOR DIFFERENT SLUG SIZES



FIGURE D-2 COMPARISON OF RECOVERIES AND WATER OIL RATIOS OF 105 CC SLUGS WITH DIFFERENT SODIUM HYDROXIDE CONCENTRATION







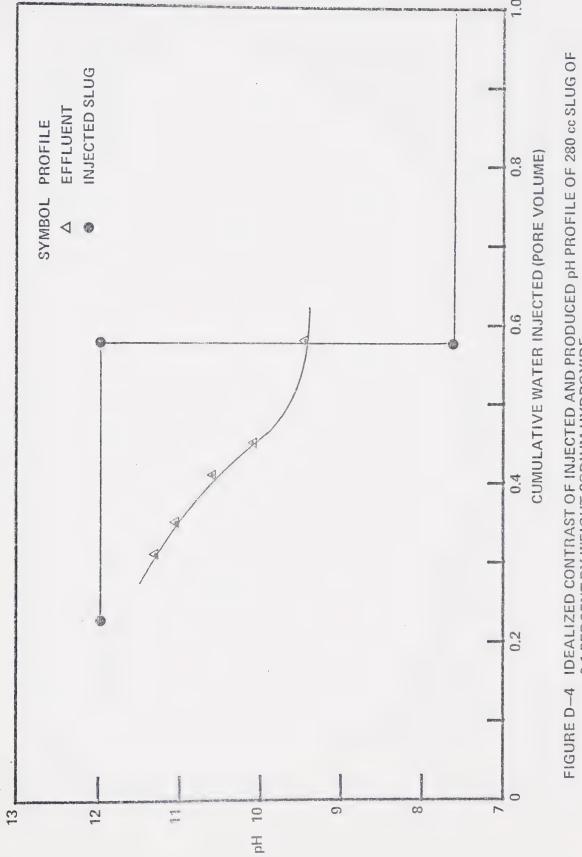


FIGURE D—4 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 280 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE



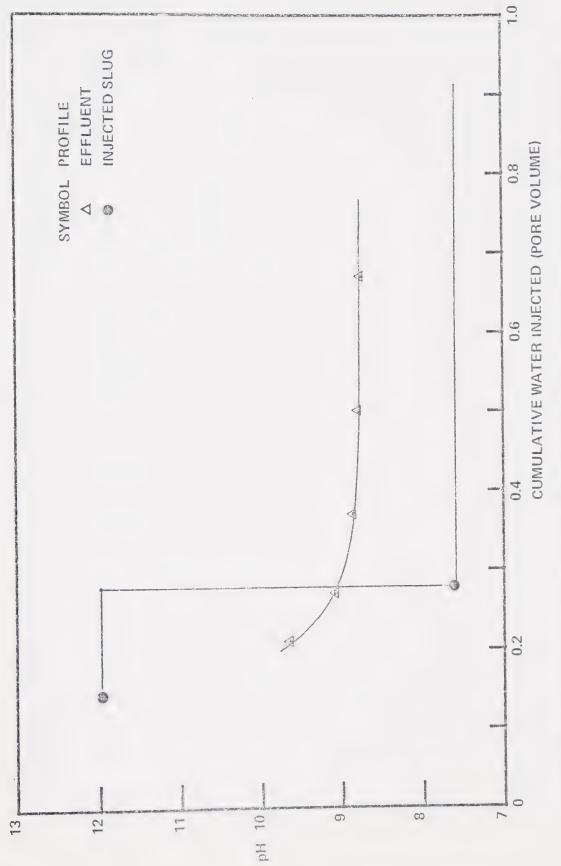


FIGURE D-5 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 105 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE



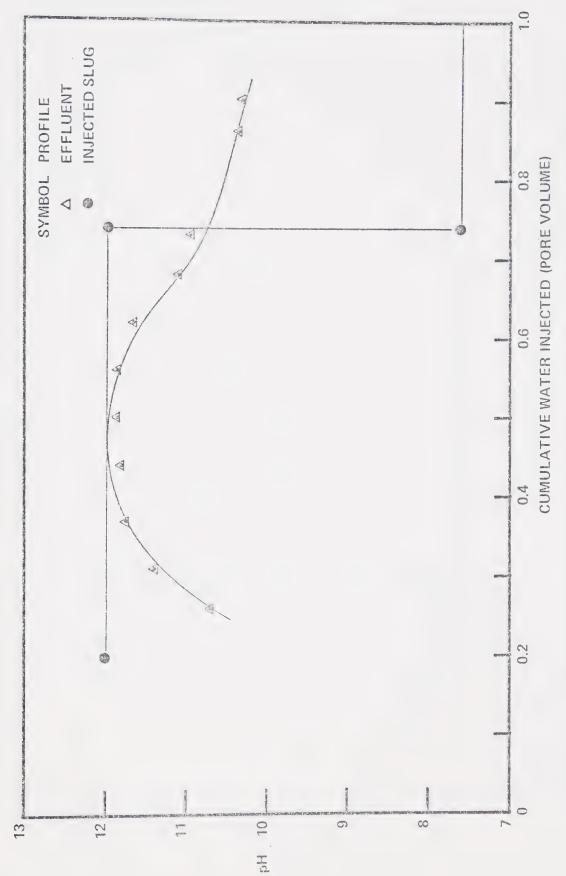


FIGURE D-6 IDEALIZED CONTRAST OF INJECTED AND PRODUCED pH PROFILE OF 402 cc SLUG OF 0.1 PERCENT BY WEIGHT SODIUM HYDROXIDE



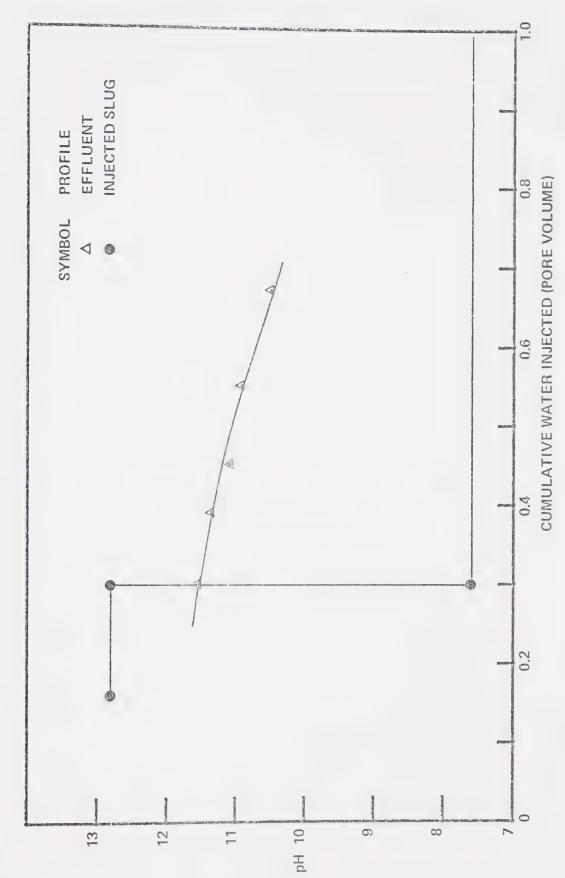


FIGURE D-7 IDEALIZED CONTRAST OF INJECTION AND PRODUCTION PH PROFILE OF 105 cc SLUG OF 1.0 PERCENT BY WEIGHT SODIUM HYDROXIDE



## APPENDIX E

RELATIVE PERMEABILITY DETERMINATIONS
FROM EXPERIMENTAL DATA



#### RELATIVE PERMEABILITY CALCULATIONS

The Welge integration of the Buckley Leveritt equation was used to calculate the relative permeabilities from displacement data as suggested by Collins 10.

$$\frac{K_{\text{NW}}}{K_{\text{NW}}} = \frac{\mu_{\text{W}}}{\mu_{\text{NW}}} \qquad \frac{1 - f_{\text{W}}}{f_{\text{NW}}}$$
 E-1

where:

 $\mu_{\rm w}$  = viscosity of wetting phase, cp,

 $\mu_{nW}$  = viscosity of non-wetting phase, cp,

 $K_{w}$  = permeability of wetting phase, md,

K<sub>nw</sub> = permeability of non-wetting phase, md,

 $f_{pw}$  = non-wetting phase fractional flow, and

 $f_{w}$  = wetting phase fractional flow.

The saturation corresponding to this ratio is the instantaneous value at the outflow phase. This saturation is calculated at the middle of the production interval by the use of Equations E-2 and E-3.

$$S_{wa} = \frac{N_{p} - \frac{1}{2} \Delta N_{p}}{PV} + S_{wi}$$
 E-2



$$S_{wd} = S_{wa} - f_0 = \frac{W_p + N_p - \frac{1}{2}(N_p + \Delta W_p)}{PV}$$
 E-3

#### Where:

S = average water saturation,

 $N_p$  = cumulative oil production, cc,

 $\Delta N_{p}$  = oil production during time step, cc,

 $S_{wi}$  = initial water saturation

PV = core pore volume, cc,

S<sub>wd</sub> = average water saturation in middle of time step

f = fractional flow, oil

 $W_{p}$  = cumulative water production, cc,

 $\Delta W_p$  = water production during time step, cc,

Results of the relative permeability calculations are presented in Table E-1 to E-3.



TABLE E-1

RELATIVE PERMEABILITY OF TEST No. 6

	S <sub>wd</sub>	0.08611	0.08848	0.11509	0.14456	0.16250	0.18282	0.18473	0.19561	0.20350	0.21029	0.20641	0.21445	0.23496	0.24237	0.24134
	S wa							0.24215							0.29742	
$\mathbb{A}_{\mathbb{R}}$	\o'\	0.0000000	0.00003	0.00045	0.00132	0.00216	19800.0	0.00378	0.004.75	0.00559	0.00642	0.00598	0.00682	0.00975	0.01126	0.01104
	Î.	1.0000	.963	.663	.402	.292	.198	0.1914	.158	.137	.122	.130	.116	.084	.073	.075
	WOR	00.	.03	0.50	.48	1100	.03	4.222	.30	.25	.16	.68	7.61	φ α	5.5	2 • 33
	W CC)	00.00	0.70	7.10	30.40	59.40	92.90	130.90	165.40	202.90	245.90	292.00	341.50	390.50	443,30	480.30
	Z (20)	50.00	68.30	80.90	96.59	108.59	116.89	125.89	132.40	138.40	144.40	151,30	157.80	1.62,30	166.49	169.49
	A W p	00.0	0.70	6.40	23.30	29.00	33.50	38.00	34.50	37.50	43,00	46.10	49,50	00.64	52,80	37,00
	A N C (cc)	50.00	18,30	12.60	15.70	12.00	20.20	00.6	6.50	6.00	6.00	6.9)	6.50	4.50	4.20	3.00

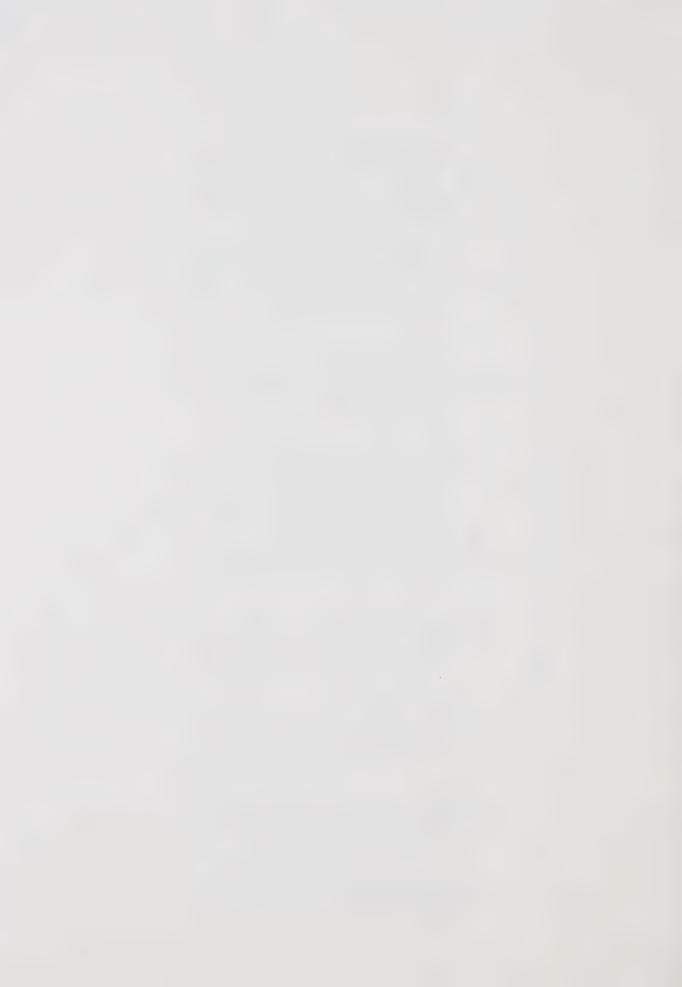


TABLE E-2

RELATIVE PERMEABILITY OF TEST No. 8

	Swd		710	710	710	159	125	641	665	805	308	989	988	141	351	371	525	0.23721	463
	S wa		.0993	.1367	.1542	,1734	.1995	.2227	.2359	.2475	.2598	.2700	.2792	.2887	.2968	.3031	.3080	0.31361	.3202
M <sub>N</sub>	o M		0.0000.0	0.000000	0.0000.0	40000.0	0.00052	0.00196	0.00223	0.00278	0.00336	0.00224	0.00447	0.00480	0.00684	0.00708	0.00933	0.00721	0.00866
	f <sub>O</sub>		00	00	00	94	62	(C)	2	24	2	a.	16				0 9		0
	WOR		000	.00	.00	.05	.59	.22	.52	. 14	.80	2.534	.06	.43	.74	.02	.56	8.166	. 8
	W	(00)		00.00	0	1.000	16.00	45.80	67.30	101.30	137.80	156.30	196.30	239.80	281.60	321.70	355.50	404.50	453.50
	Za	(cc)	47.00	62.00	76.00	94.00	119.20	132.60	141.10	151,90	161.49	168,79	176.69	184.69	190.09	195.09	198.29	204.29	219.29
	D W D	(00)	00.0	00.0	00.0	1.00	15.00	29.80	21.50	34.00	36.50	18,50	40.00	43.50	41.80	40 . 10	33.80	00.65	00.64
	NO	(00)	47.00	15.00	14.00	18.00	25.20	13.40	8.53	10.79	0.60	7.30	7.89	R.00	5.4)	5.00	3.27	6.00	5.00



TABLE E-3

RELATIVE PERMEABILITY OF TEST No. 9

f O
C
C
000
30
29
21
0.2142
00
16
13
3
-



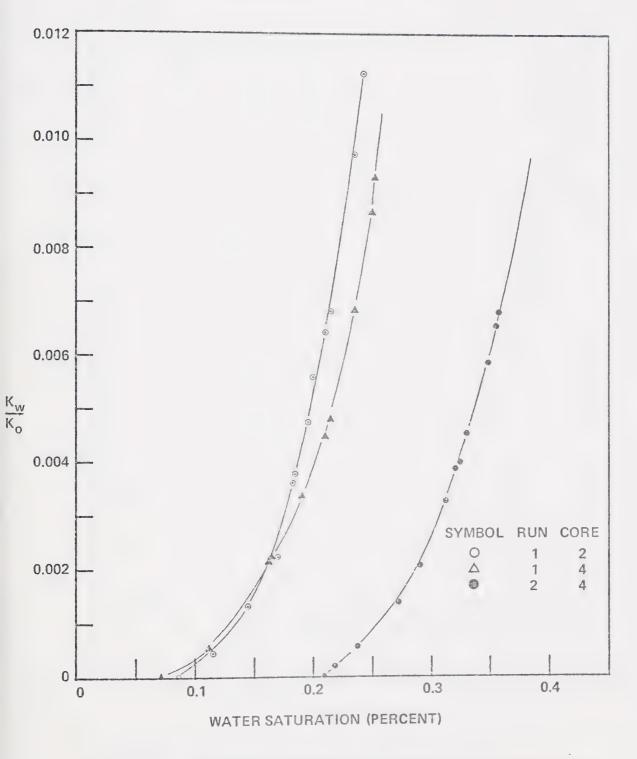
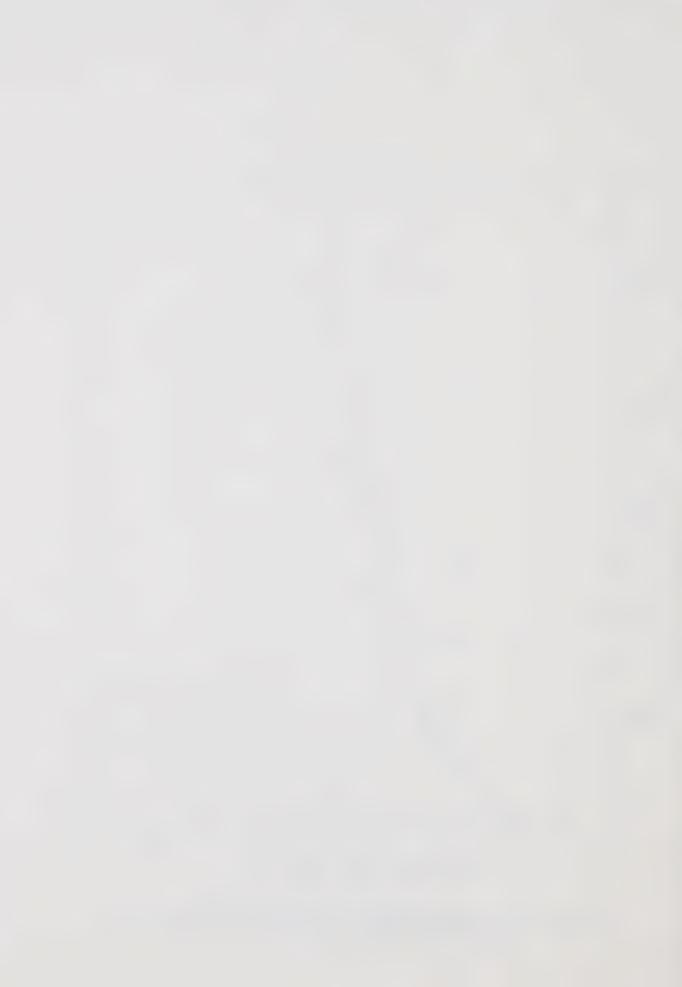


FIGURE E-1 THE EFFECT ON RELATIVE PERMEABILITY OF MULTIPLE DISPACEMENT TESTS ON A CORE



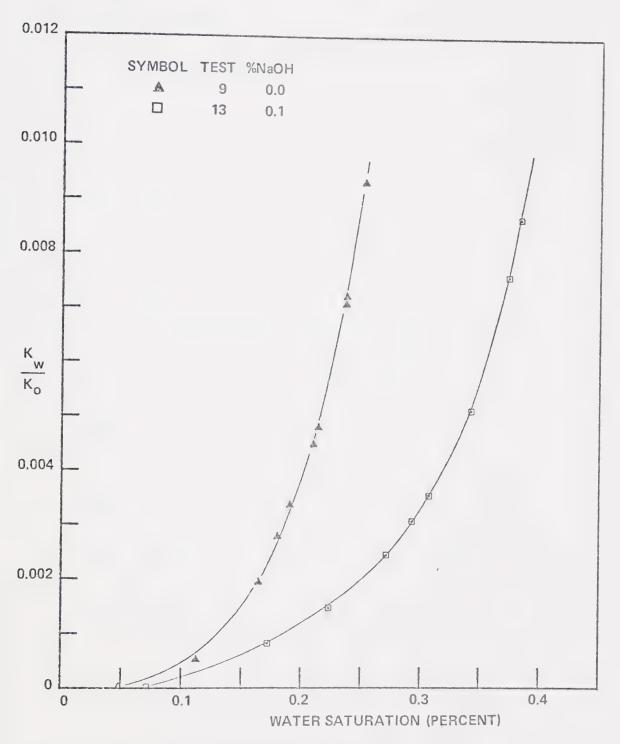


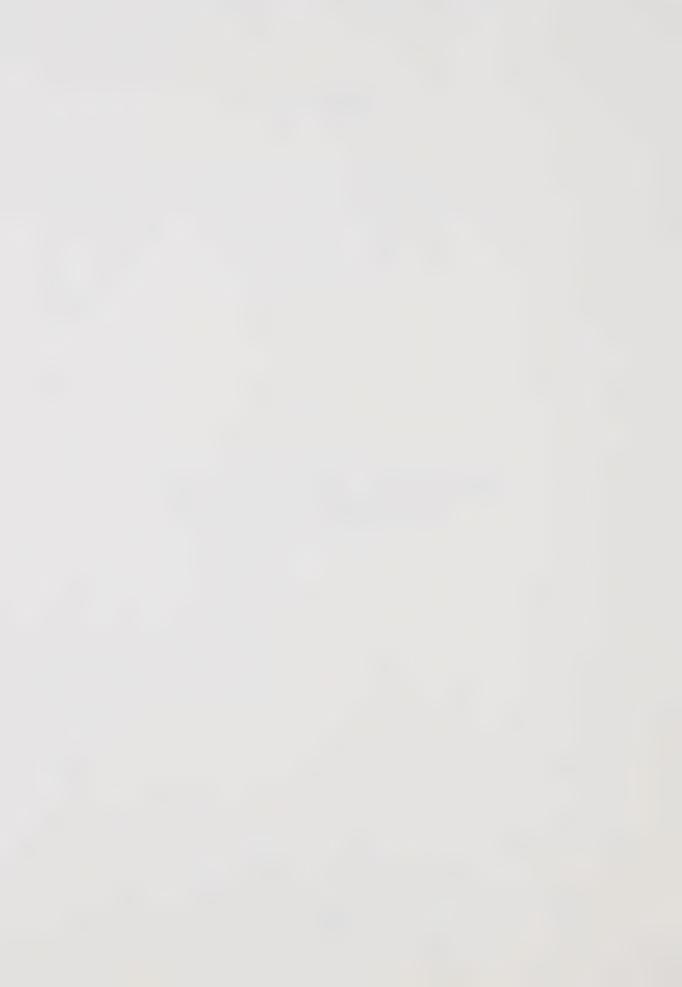
FIGURE E-2 THE EFFECT OF SODIUM HYDROXIDE ON RELATIVE PERMEABILITY



### APPENDIX F

APPLICATION OF EXPERIMENTAL RESULTS

TO AN IDEALIZED FIELD CASE



#### IDEALIZED OIL FIELD PROJECT

### Initial Conditions

Ø = 40%

h = = 10 feet

Area = 40 acres

S<sub>wi</sub>

= 10 percent

 $B_{0i} = 1.25$ 

\*pw

= 1.0859

\*0.1 percent by weight sodium hydroxide.

### Initial Oil-In-Place

$$N = \frac{7758 \, \text{Ø} \, (1 - S_{\text{Wi}}) \, \text{Area h}}{B_{\text{Oi}}}$$

$$N = \frac{7758 (0.4) (1 - 0.1) (40) (10)}{1.25}$$

N = 893,721 ST Bbls.

## Linear Laboratory Model

Initial Oil-In-Place

750 cc

Slug Size

300 cc

Concentration Sodium

Hydroxide

0.1 percent by weight

Recovery at W.O.R. of 10 43% of I.O.I.P.

Recovery Factor = Oil Recovered
Sodium Hydroxide Injected

Recovery Factor =  $\frac{750cc(0.43)}{300cc(0.001)(1.0839)} = 990 \frac{cc \text{ oil}}{gm \text{ sodium}}$ hvdroxide

Recovery Factor = 2:519 Bbls. Oil/lb. Sodium Hydroxide



## Conventional Water Flood Recovery

Recovery of I.O.I.P.

$$(At W.O.R. = 10) = 10%$$

 $893,721 \times 0.1 = 89,372 \text{ ST Bbls.}$ 

# Sodium Hydroxide Slug Field Project Recovery (assume

linear flow, 50% volumetric sweep)

$$893,721 \times 0.43 \times 0.5 = 192,150 \text{ STB}$$

Sodium Hydroxide Required

192,150/2.519 = 67,617 lbs.

#### Increased Recovery Using Sodium Hydroxide

192,150 - 89,372 = 107,778 STB

# Slug Volume Required

225,000 Bbls. water

## Idealized Injection Rates

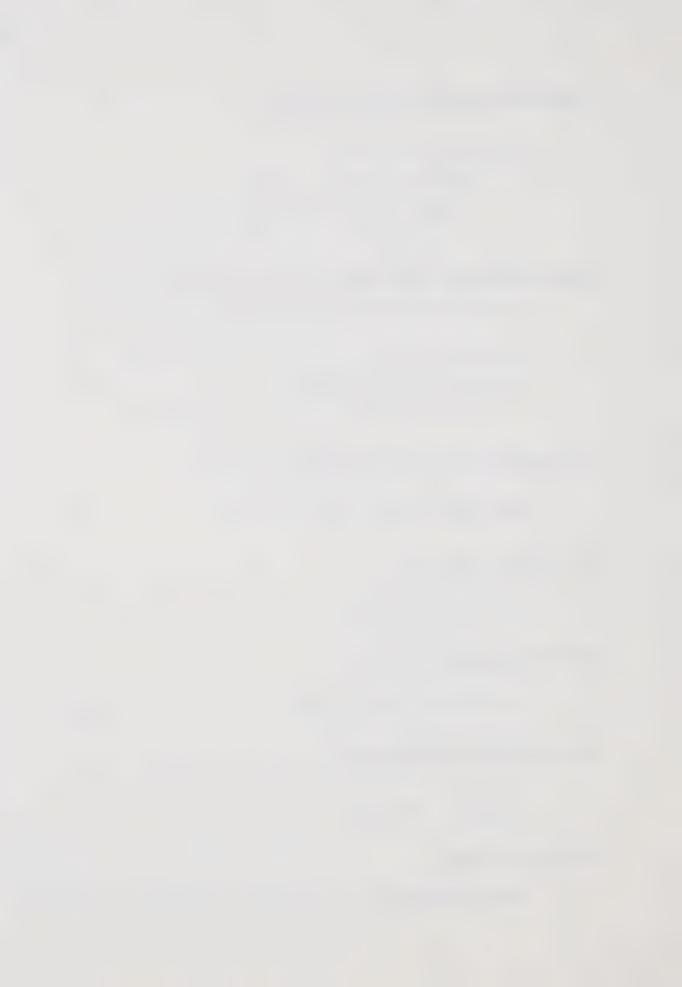
1,000 Bbls. water per day

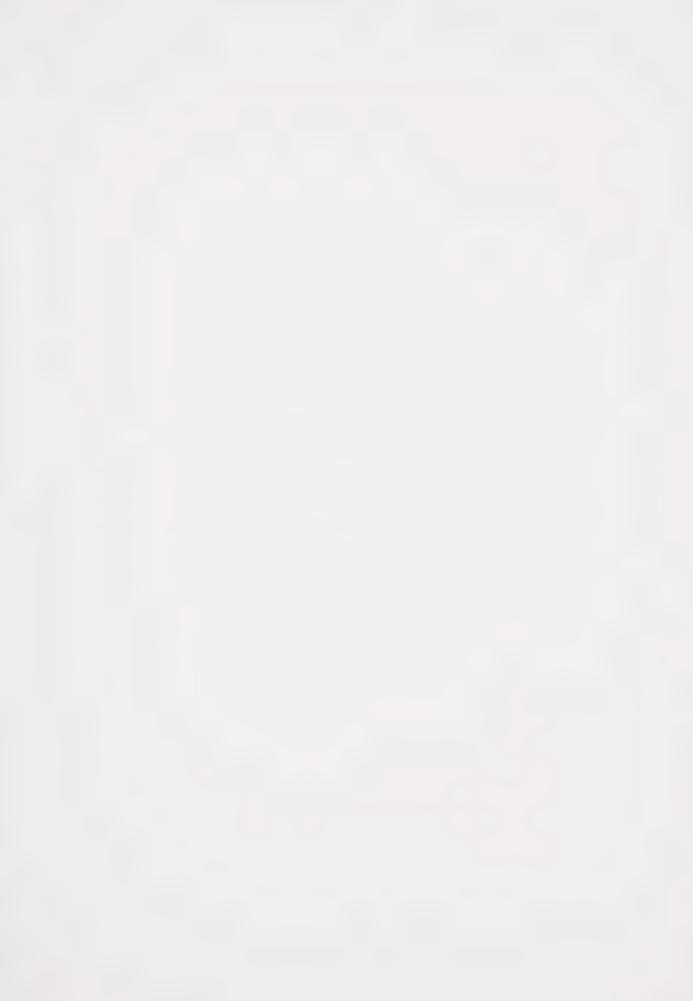
# Time Required to Inject Slug

$$\frac{225,000}{1,000} = 225 \text{ days}$$

# Economic Estimate

Sodium Hydroxide cost (50¢/lb.) 67,617 lbs. = \$33,809













B30170